SINTEF

SINTEF Materials and Chemistry

P.O.Box: 4760 Sluppen
Address: NO-7465 Trondheim, NORWAY
Location: Sem Sælands vei 2A
Telephone: +47 4000 3730
Fax: +47 73 59 69 95

Enterprise No.: NO 948 007 029 MVA

SINTEF REPORT

TITLE

H&E TQP ID1:
Establish sampling and analytical procedures for potentially harmful components post combustion amine based CO_2 capture

Subtask 5: Establish analytical procedures

FM07-AJZ00-S-RA-0003-03

AUTHOR(S)

Kolbjørn Zahlsen, Kai Vernstad, Torunn Holten, Anders Brunsvik, Aslak Einbu, Bernd Wittgens, Per Oscar Wiig

CLIENT(S)

Gassnova SF, Dokkveien 10, N-3920 Porsgrunn, Norway
Jens Solli, Audun Gangstad

REPORT NO.	CLASSIFICATION	CLIENTS REF.	
SINTEF F 18774	Confidential	CCM/257430101	
CLASS. THIS PAGE	ISBN	PROJECT NO.	NO. OF PAGES/APPENDICES
Confidential		80157001	28/5
ELECTRONIC FILE CODE		PROJECT MANAGER (NAME, SIGN.)	CHECKED BY (NAME, SIGN.)
		Kolbjørn Zahlsen K. Zahlsen	Paal Skjetne for Ole Wærnes
FILE CODE	DATE	APPROVED BY (NAME, POSITION, SIGN.)	
	2011-04-28	Trond E. Ellingsen, Research Director Trond Ellingsen.	

ABSTRACT

The objective of H&ETQP/Amine1 is to have well documented analytical procedures for potentially harmful components from post combustion amine based CO2 capture in order to enable complete emission characterization.

Results: 1) For all 21 compounds listed in the scope of work, methodology has been developed and validated, 2) Method descriptions have been made in accordance with ISO 17025, 3) Validation reports have been made in accordance with ISO 17025. 4) For the nitrosamines, three different types of methods have been developed: i) quantitative methods for secure identification and sensitive quantification based on LC-MS-MS-QQQ, ii) screening methods for detection and quantification based on GC-MS-NCD (TEA) detection and iii) a group method giving total amount of nitrosamines based on release of NO (the nitroso group) after treatment with CuCl and HCl in a closed vial followed by subsequent analysis of NO on GC-MS-NCD. 5) In an artefact study nitrosation has been studied experimentally and the potential formation of nitrosamines during instrumental analysis has been eliminated. 6) An interaction study has been performed to ensure that interaction/interference does not occur between the compounds studied. 7) A stability study has been performed for nitrosamines, amides and aldehydes. 8) Flue gas samples have been made experimentally in the VOCC rig, the flue gas samples have been sampled by three different sampling systems, and the results from the samplings are given. 9) A cross-validation of methodology has been made in collaboration with NILU.

KEYWORDS	ENGLISH	NORWEGIAN
GROUP 1	Chemistry	Kjemi
GROUP 2	Analysis	Analyse
SELECTED BY AUTHOR	CO_2 capture	CO_2 innfanging
	Chemical analysis	Kjemisk analyse
	Analytical methods	Analysemetoder

Table of Contents

Executive summary

Methodology has been developed and validated for *quantitative analysis* of 21 compounds related to amine based carbon capture, with a main focus on methodology for 7 nitrosamines and 4 alkylamines. The list of compounds comprise amines (monoethanolamine (MEA), diethanolamine (DEA), piperazine (PZ), 1,2-diaminoethane (EDA), amino-2-methyl-1-propanol (AMP) and N-methyldiethanolamine (MDEA)), ammonia, aldehydes (formaldehyde and acetaldehyde), amides (formamide and acetamide), alkylamines (methylamine, ethylamine, dimethylamine and diethylamine) and nitrosamines (N-Nitrosodimethylamine (NDMA), N-Nitrosodiethylamine (NDEA), N-Nitrosomorpholine (NMOR), N-Nitrosopiperidine (NPIP), N-Nitrosodiethanolamine (NDELA), N-Nitrosopiperazine (NPZ) and 1,4-Dinitrosopiperazine (DNPZ)). The analytical methods are based on liquid chromatography – triplequadrupole mass spectrometry (LC-MS-MS-QQQ) except for the alkylamines which are based on gas chromatography – mass spectrometry (GC-MS). *The instrumental sensitivities for all these methods are in the low- or sub microgram per liter range. The mass spectrometric methodology used in this project represents state of art with respect to the combination of secure identification and high sensitivity.*

A *screening method* has been developed for nitrosamines. This method is based on gas chromatography with nitrosamine-specific detection with thermal energy analyzer (TEA), also known as nitrogen chemiluminescence detection (NCD). The GC-MS-NCD screening method allows for simultaneous detection with mass spectrometry (MS) for confirmation of identity of compounds detected by NCD. *The instrumental sensitivity of the GC-MS-NCD method is in the low mg per litre for a typical nitrosamine. The NCD detector can be used as the only detector, but combination with MS enhances the possibility of identification of compounds detected by the NCD detector.*

A *group method* for nitrosamines has been developed. The group method is based on chemical denitrosation with CuCl / HCl in a closed vial with formation of NO gas from the nitroso group and direct analysis of the released NO gas by head space analysis from the closed vial with GC-NCD. *The group method is very simple to perform and has a high instrumental sensitivity in the sub-microgram per litre range.*

The above methods are developed for aqueous *samples* of flue gas, wash water and amine solvents, with flue gas as a major target. Due to the risk of artefact formation during sample preparation (see below), the main strategy for sample preparation has been to minimize the sample manipulation and especially exposure to chemicals and low pH, which may affect the analytical result. Therefore, the combination of high instrument sensitivity with direct injection

of the sample, if necessary assisted by a pre-dilution for samples with very high amine concentration, has been the strategy to avoid artefact formation as a result of sample preparation. A consequence of dilution is reduced sensitivity for samples with high amine concentrations like solvent samples, however, this can be compensated by the use of a clean-up / concentrating step performed by a neutral liquid-liquid-extraction prior to the instrumental analysis.

The most serious and challenging *artefact* problem for nitrosamine analysis is nitrosation, i.e. artefactual formation of nitrosamines by reactions between secondary amines and nitrogen oxides like nitrite. The nitrosation reactions are normally facilitated by acidic pH, therefore all steps of the LC-MS-MS-QQQ methods for nitrosamines are operated at neutral pH (pH 7-8) with ammonium acetate mobile phase buffer during chromatographic separations. The basis for this principle is laboratory tests performed with secondary amines and nitrite showing no nitrosation with ammonium acetate and elimination of the theoretical possibility of nitrosamine formation within the LC-MS-MS-QQQ system. For the GC-MS-NCD screening method, experiments have been performed with secondary amines and nitrite. In these experiments, no artefactual formation of nitrosamines has been observed, although special attention has been directed to the theoretical possibility of nitrosamine formation inside the hot injector of the GC system. For the group method, dissolved nitrite in the sample will lead to the formation of NO by the CuCl / HCl treatment, in addition to the NO released from the nitrosamines, and potentially lead to a false positive result or an overestimation of the total nitrosamine concentration. However, the problem with NO formation from nitrite is eliminated by the addition of sulfamic acid to the sample before reaction with CuCl / HCl. The mechanism behind this is that sulfamic acid act like a nitrite scavenger and removes the nitrite by chemical conversion. The preventive effect of sulfamic acid has been verified experimentally in laboratory tests.

Analytical *interactions* between solvent amines and nitrosamines has been a major challenge during method development, as presence of amines may reduce the analytical sensitivity e.g. by ion suppression. For the quantitative LC-MS-MS-QQQ methods this problem was minimized by the use of analytical columns and mobile phases that resulted in elution of the nitrosamines before the amines, which is very favourable for sensitivity. This “reversed” elution order was possible by the use of a newly developed type of analytical column with pentafluorobenzene as stationary phase. With this type of columns, it is possible to achieve a controlled “group” separation between trace nitrosamine analytes and the amines by systematic alteration of the mobile phase solvent composition. The methodology and the controlled group separation is very valuable to avoid interferences between analytes and major compounds like solvent amines.

Stability studies in water have shown that the nitrosamines have a good long-term stability, that temperatures between -20ºC and +50ºC are tolerated, that nitrosamines can be stored in glass vials and HDPE vials, however, results indicate that samples should be protected against light.

The results from the other compounds tested (amides and aldehydes) indicate lower stability, and further stability studies are needed.

The procurement of *flue gas samples* and testing / demonstration of three *different sampling systems* was performed by experiments with a specialized test rig, the VOCC (Validation of CO_2 Capture) rig at SINTEF. The sampling systems were based on isokinetic sampling with a combined condensate / impinger train, and a classic impinger train, both with sorbent solution (0.1M H_2SO_4) and, finally, a two-stage (+2ºC / -85ºC) condensate trap. The results from the VOCC experiment showed consistent results between the three different systems for the amines, ammonia, nitrosamines and alkylamines. The results are promising for the use of the condensate trap as a possible sampling principle.

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 is to have well documented analytical procedures for potentially harmful components from post combustion amine based CO_2 capture to enable a complete emission characterisation. The matrices will be various amines for CO_2 capture, wash water and gaseous samples where the analyte(s) are collected on solid or liquid sorbents.

The work can be based on available literature, standard methods and/or in-house developments.

2 Scope of work

The scope of work of Subtask 5 is to establish validated methods for chemical analysis of amines and degradation products as ammonia, aldehydes, amides, alkylamines and N-nitrosamines. Special emphasis should be on N-nitrosamines and alkylamines.

For nitrosamines, the proposed procedures should include the following 3 approaches:

i) a quantitative method for specific N-nitrosamines with high sensitivity
ii) a screening method where all nitrosamines in the sample will be detected and quantified
iii) a group method giving total amount of N-nitrosamines.

For all procedures, detailed descriptions of procedures and validation must be given. The analytical methods are to be tested with synthetic flue gas samples procured by Contractor.

3 Methodological approach / Sub-activities

As a methodological approach to the scope of work, Subtask 5 was divided into 6 different sub-activities. These sub-activities were:

1) Procurement of samples from the VOCC rig
2) Development of analytical methods for amines, ammonia, aldehydes, amides, alkylamines and nitrosamines
3) Development of three different approaches for nitrosamines
    a. Quantitative method for specific nitrosamines with high sensitivity
    b. Screening method where all nitrosamines in the sample will be detected and quantified
    c. Group method giving total amount of nitrosamines.
4) Artefact study
    a. Nitrosation
    b. Interactions
5) Stability study
6) Validation study

4 Results

The results are reported for each sub-activity as six separate Chapters (4 to 9). The report contains five appendices (Appendix 1 to 5). Appendix 1 reports the methodology used for procurement of flue gas samples by use of the VOCC rig (Validation of CO_2 Capture). These samples were needed for method validation. Appendix 1 also reports the use of three different sampling methodologies and the analytical results from the samplings. Appendix 2 is the method descriptions as described in ISO 17025 Chapter 5.4.4. Appendix 3 is a description of the validation of the methods as described in ISO 17025 Chapter 5.4.5. Appendix 4 is the results from the stability study, and Appendix 5 is the results from an analysis of a set of unknown samples from SINTEF analyzed by NILU.

4.1 Procurement of flue gas samples from the VOCC rig

In order to produce a gas sample reflecting a relevant flue gas sample from an amine absorber, the VOCC test rig was applied in order to circulate synthetic wash water over a packed column counter-currently with CO_2 containing air in a closed and temperature controlled system. Gas-liquid equilibria enable a controlled, realistic gas flow downstream the column, with a realistic content of water, CO_2, ammonia and organic compounds of interest.

It was of great importance for the Amine1 project to have access to flue gas sample matrix for an evaluation of the methodology developed. To get a flue gas matrix relevant for to the solvent systems given in the ITT, it was decided to generate a synthetic flue gas sample that covered solvents A and B of the solvent systems given in the ITT, (Solvent A = 30% MEA and solvent B = 25% AMP and 15% piperazine) and the majority of the other compounds given in Appendix D – Examples of specific substances in the various groups; amines, ammonia, aldehydes, amides, alkylamines and nitrosamines.

The VOCC rig is described in detail in Appendix 1. The VOCC rig has a column with a 5 meter packed section where it is possible to perform controlled experiments with generation of synthetic flue gas from a wash water with a defined composition. On top of the wash water section, there is a 5 meter long straight section that allows isokinetic sampling of the gas. Prior to the generation of flue gas, the VOCC rig was modified to allow simultaneous gas sampling using three different sampling systems/principles. On the basis of the results from the Amine1 subtask 2 – Manual sampling, it was decided to use the following three sampling systems: 1) ISOK4 from Environment S.A. Germany, an automated system for isokinetic sampling with automatic flow control, a condensate step and a H_2SO_4 filled impinger train, 2) a “classic” H_2SO_4 filled

impinger train and 3) a two-stage (+2°C and -85°C) condensate trap. During sampling the VOCC was operated with wash water with the following composition, shown in Table 4.1 below:

Table 4.1: Composition of wash water in VOCC experiment for procurement of flue gas samples.

Group or compound	Compound	Concentration
Amines	MEA	1 g/L
	Piperazine	1 g/L
	AMP	1 g/L
Ammonia	Ammonia	10 mg/L
Aldehydes	Formaldehyde	1 mg/L
	Acetaldehyde	1 mg/L
Amides	Formamide	1 mg/L
	Acetamide	1 mg/L
Alkylamines	Methylamine	1 mg/L
	Ethylamine	1 mg/L
	Dimethylamine	1 mg/L
	Diethylamine	1 mg/L
Nitrosamines	NDMA	300 µg/L
	NDELA	300 µg/L

The selection of compounds and the concentrations chosen were considered as realistic for a wash water, and the concentrations of each compound was monitored in wash water during the VOCC experiment. The rationale behind the selection of the sampling methods were that 1) amines and ammonia are captured in solutions of H_2SO_4 and that 2) it has been observed that several compounds (including nitrosamines) have been found in cold traps for drying of flue gas during sampling. The synthetic wash water was circulated over the column with a controlled temperature of 50ºC and a counter current superficial gas flow of 3 m/s in the main column.

The results from analysis in wash water and in flue gas samples are given in Appendix 1.

It can be concluded that the VOCC experiment has given a successful procurement of three different types of relevant flue gas samples. The flue gas samples reflect relevant compositions of wash water constituents at realistic concentrations. The VOCC experiment has been performed under controlled conditions and the flue gas samples are therefore relevant for validation of the methodologies for the same and other constituents in flue gas.

4.2 Development of analytical methods for amines, ammonia, aldehydes, amides, alkylamines and nitrosamines

4.2.1 Amines

SINTEF has developed analytical methodology for the amines monoethanolamine (MEA), diethanolamine (DEA), piperazine (PZ), 1,2-diaminoethane (EDA), amino-2-methyl-1-propanol (AMP) and N-methyldiethanolamine (MDEA). The methods are based on liquid chromatography coupled with triplequadrupole mass spectrometry (LC-MS-MS-QQQ). The methods are based on reversed phase chromatography and atmospheric pressure electrospray ionization (ESI). Method descriptions are given for each amine in Appendix 2 and validation data are given for each amine in Appendix 3.

The LC-MS-MS-QQQ methodology provides a very high sensitivity for amines due to the fact that amines are easily protonated to give efficient ionization. This is important for sensitivity. The use of LC separation instead of GC is useful due to the fact that amines, and especially alkanolamines, have poor chromatographic performance on most GC columns. The MS detection principle provides a very high specificity due to the fact that unique masses and fragments are monitored for more than one transition.

4.2.2 Ammonia

SINTEF has developed a method for analysis of low concentrations of ammonia in aqueous solutions by GC-MS. This is the same method as the one described later for alkylamines. The method is based on direct derivatization of ammonia with benzene sulfonyl chloride (BSC) in aqueous solution. Method descriptions are given in Appendix 2 and validation data in Appendix 3.

The GC-MS method provides a very high sensitivity due to the high response of the derivative and a high specificity due to the mass spectrometric detection principle.

Derivatization can be performed directly on a sample taken from an absorption (or condensate) solution. The derivatization product has a much stronger MS response than underivatized ammonia, but with the high specificity of the MS. In addition, the product of the derivatization

reaction gives a molecule with relatively low polarity that makes derivatized ammonia extractable from water with an organic solvent. Therefore, extraction from larger volume of aqueous solution into a smaller volume of organic solvent (that can easily be further reduced by evaporation) allows for a concentrating step that can enhance the sensitivity for ammonia by GC-MS by a factor of one thousand (or more).

4.2.3 Aldehydes

SINTEF has developed LC-MS-MS-QQQ methodology for formaldehyde and acetaldehyde in aqueous solutions. The methodology is based on derivatization with dinitrophenylhydrazine (DNPH) and on reversed phase chromatography and atmospheric pressure electrospray ionization (ESI). Method descriptions are given in Appendix 2 and validation data in Appendix 3.

Derivatization of the aldehydes with DNPH gives a higher response by LC-MS-MS-QQQ than the underivatized aldehydes. The mass spectrometric methods give a much higher specificity compared to older LC-UV methods.

Aldehydes are reactive species that undergoes reactions with several other classes of compounds. Examples are reactions with water to form hemiacetals or acetals, with amines to form imines, with hydroxyl amines to form oximes, with semicarbazides to form semicarbazones and with hydrazines to form hydrazones. In addition, a large number of other reactions are possible due to the reactive carbonyl groups of the aldehydes. Derivatization with DNPH protects the aldehydes from unwanted reactions with other compounds.

4.2.4 Amides

SINTEF has developed LC-MS-MS-QQQ methodology for formamide and acetamide. The methods are based on reversed phase chromatography and atmospheric pressure electrospray ionization (ESI). Method descriptions are given in Appendix 2 and validation data in Appendix 3.

Liquid chromatography with triplequadrupole mass spectrometry (LC-MS-QQQ) is the methodology that has given the best performance with respect to sensitivity and specificity for these compounds.

4.2.5 Alkylamines

SINTEF has developed a GC-MS method for methylamine, ethylamine, dimethylamine and diethylamine based on derivatization with beznyl sulfonyl chloride (BSC) (this is the same method that is used for ammonia above). Method descriptions are given in Appendix 2 and validation data in Appendix 3.

The derivatives of the alkylamines have an increased response by GC-MS that allows detection with an instrumental sensitivity of < 10 µg/L by direct injection. Moreover, the derivatives formed are less polar than the alkylamines and they can therefore be extracted from an aqueous water phase into an organic solvent phase with a lower volume, and thereby be concentrated. The solvent extract can be further reduced in volume, and the sample can therefore be more concentrated. Due to these processes, a concentrating factor of more than one thousand can be achieved.

4.2.6 Nitrosamines

SINTEF has developed methodology for nitrosamines for *quantitative* analysis based on LC-MS-MS-QQQ, for *screening* analysis based on GC-MS-NCD (Nitrogen Chemiluminesence Detection) and for *group* specific detection based on the conversion of the nitroso group to NO by a reaction with CuCl and HCl. The NO formed is subsequently captured in a head space vial. The NO formed within the head space vial is injected onto a GC-MS-NCD system identical with the one used for screening analysis.

These three methods for nitrosamines are described in Chapter 5 below.

5 N-Nitrosamines

5.1 Quantitative method for specific nitrosamines with high sensitivity

SINTEF has developed LC-MS-MS-QQQ methodology for quantiation of the nitrosamines N-Nitrosodimethylamine (NDMA), N-Nitrosodiethylamine (NDEA), N-Nitrosomorpholine (NMOR), N-Nitrosopiperidine (NPIP), N.Nitrosodiethanolamine (NDELA), N-Nitrosopiperazine (NPZ) and 1,4-Dinitrosopiperazine (DNPZ). Method descriptions are given in Appendix 2 and validation data in Appendix 3.

LC-MS-MS-QQQ is the methodology selected for quantitative analysis of nitrosamines with the highest possible sensitivity and specificity. The instrumental sensitivity is for most nitrosamines in the low or sub- microgram per liter (µg/L) level. The specificity is very high because the use of one, or where applicable, two specific transitions makes it very unlikely that another compound is incorrectly identified as the nitrosamine. In addition, the use of two transitions makes it possible to apply the same (or similar) criteria and rules for identification that is being used for identification within the fields of forensic chemistry. Here, identification is based on correct retention time, presence of signal (peak) on two different transitions and the correct (within specific allowed limits) signal ratio between the two transitions. Principally, and due to the importance of the nitrosamines as potentially harmful components, it should be aimed to apply the same quality criteria and rules for identification and quantitation as for the field of forensic chemistry.

The nitrosamine methods developed by SINTEF share one common important chromatographic feature, which is the use of the Discovery HS-F5 analytical column. This column is different from ordinary reversed phase columns because of the utilization of a new stationary phase which contain aromatic rings substituted by five fluorine atoms. Unlike ordinary C18 columns, the HS-F5 phase produces an elution order where the nitrosamines can be forced to elute before the amines. This is extremely beneficial because the method will be applied to samples that contain solvent amines in a molar ratio up to 10 orders of magnitude more than the nitrosamines (i.e. molar vs. nanomolar concentrations). If the amine elutes from the analytical column before the nitrosamine, this would inevitably cause a tailing amine peak with unwanted presence of amine when the nitrosamine elutes. The simultaneous presence of high concentration of amine will cause ion suppression and decrease the sensitivity for the nitrosamine. This problem is eliminated by the use of the HS-F5 column. By systematic alterations of the mobile phase composition, the separation between different nitrosamines and different solvent amines can be systematically optimized.

Nitrosation of secondary amines by nitrogen oxides within the analytical instrument is a major concern in this project. It is known that acidic conditions generally enhance nitrosation, although different pH optima for nitrosation may exist. Our strategy has been to avoid exposure of the sample to any acidic environment. Control of pH is essential in all LC systems where the analytes have basic or acidic functional groups. We have tested the effects of different mobile phase constituents, and found that no nitrosation occurs as result of reactions between nitrite and the secondary amines relevant for the nitrosamines included in this study (dimethylamine, ethylamine, morpholine, piperidine, diethanolamine, piperazine and n-nitrosopiperazine). Tests

and the results from the tests are described in more detail in ‘Chapter 6: Artefacts’, later in this report.

5.2 Screening method for detection and quantification of nitrosamines

SINTEF has developed a GC-MS-NCD screening method for nitrosamines. The GC method is based on the use of the NCD detector (nitrogen chemiluminescence detector) in combination with mass spectrometry. The NCD detector is a further development of the TEA detector (thermal energy analyzer) and this is the only known detection principle that is developed as a specific detector for nitrosamines. Method descriptions are given in Appendix 2 and validation data in Appendix 3.

The principle behind the NCD detector is that when a nitrosamine is heated to a certain temperature (400 to 500ºC), the chemical bond between the two nitrogen atoms (N-NO) of the nitroso group will be thermally broken. The result of this is that a nitrosyl radical ion is formed, and this ion is reacted with ozone to form an electronically excited nitrogen dioxide. The excited nitrogen dioxide decays quickly to its ground state while light is being emitted (800 nm). The emitted light is measured by a photo mulitiplicator tube (PMT).

With the GC-MS-NCD, the GC column effluent is splitted and led to an MS detector in parallel with the NCD detector. As a result of this, both NCD and MS chromatograms are produced simultaneously. The MS detector is operated in the scan mode, producing compound specific spectra which are searchable on the instrument’s spectrum database. This makes it possible to verify if a peak detected by the NCD detector is a nitrosamine or not. This is very useful because some nitro compounds have been shown to give response with the NCD detector and therefore erroneously become identified as a nitrosamine.

The instrumental sensitivity of the NCD detector for nitrosamines is lower than with LC-MS-MS-QQQ. As a general rule, nitrosamines can be detected at concentrations above 100 µg/L with NCD, and identified by MS above 500 µg/L.

The GC-MS-NCD methodology is developed with a GC-column that accepts injection of aqueous samples as flue gas sorption solutions samples and wash water samples by direct injection. Due to high content of amine, solvent amine samples normally would require dilution by a factor of 10–100 before injection.

It has not been studied systematically which compounds or groups/classes of compounds that give false positive or false negative results with the NCD detector. From own studies we know that 3 nitramines (methylnitramine, ethylnitramine and dimethylnitramine) give a reasonable NCD response while other nitramines (MEA-nitramine, AMP-nitramine and PZ-nitramine) give a low NCD response. We suggest that these compounds are checked out further with respect to their NCD responses since this class of compounds seems to be of specific interest in amine related carbon capture.

5.3 Group method for nitrosamines

SINTEF has developed a group method for measurement of total amount of nitrosamines. The method is based on the principle published by Wang. et al. 2005 where nitrosamines are measured after chemical denitrosation and subsequent chemiluminescence detection. Total nitrosamines is measured as released NO gas (from the nitroso group of the nitrosamine) by TEA (NCD) after treatment of the sample with CuCl and HCl. The method reported by Wang has been modified with respect to the sample preparation step as the denitrosation step is performed in a closed 2 mL sample vial at 70°C after capping. The NO gas released is injected directly from the head space gas phase (above the liquid) of the vial into a GC-MS-NCD instrument configured identically as for the screening method described above. As for the screening method above, a nitrosyl radical is generated inside the burner and the sum of nitrosamines is measured as sum NO released from nitrosamine spiked calibration samples. With this principle, NO produces one peak with the NCD detctor. Calibration should be performed with a standardized mix of nitrosamines or one specific nitrosamine representative for other nitrosamines. We have performed analyses of nirosamines after the reaction and found no remaining nitrosamines. We have also analyzed the corresponding secondary amines and identified these as the product of the denitrosation reaction.

Wang tested the selectivity of the method for different nitroso-compounds. High release of NO was found from the nitrosamines NDPA, NPYR and N-nitrosodiphenylamine and the tobacco specific nitrosamines NNN and NNK and also from related compounds as nitrosamides (MNU and MNNG). Possible interfering compounds like O-nitroso, C-nitroso, S-nitroso and C-nitro compounds were also tested. Except for the S-nitroso compounds, the interferences from these compounds were very low. Of special concern in amine related analysis is nitrite. Wang found that sodium nitrite would give release of NO which erroneously would give a false positive result with the group method, however, this was completely eliminated by addition of sulfamic acid to the sample before testing. The preventive effect of sulfamic acid (as a NO_2 scavenger) has been confirmed by us. We have also tested if NO is released from nitrate with the CuCl / HCl method.

A very small amount of NO was found at the highest concentration of nitrate added (70 mg/L corresponding to 1.1 mM).

We have tested the group method for nitrosamines in experiments with five different nitramines (MEA-nitramine, AMP-nitramine, PZ-nitramine, MA-nitramine and DMA-nitramine). The results show that none of these nitramines interfere with the group method by production of NO in the sample preparation process for total nitrosamine.

As observed also by Wang, we found a slight/moderate reduction of the nitrosamine content after treatment with sulfamic acid. At present, the cause of the reduction is not known, and this should be investigated experimentally with a concomitant analysis of secondary amine and nitrite.

Although the work of Wang is thorough, and thus represent a solid basis for the method presented by us, it should be remembered that the methodology of Wang was developed for analysis of total nitrosamines in water extracts of food products, cosmetics and urine samples. Further testing with flue gas samples may therefore be required to get a full elucidation of possible interferences from amine systems. These tests should be performed in controlled experiments where the nitrosamines are analyzed systematically and in parallel with all three methods for nitrosamines; the quantitative method, the screening method and the group method.

We have validated the CuCl/HCl method with samples from the VOCC rig. The analysis of these samples show that it is possible to detect total nitrosamine as NO and the quantitative result (calibrated with NO released from NDMA) found is in accordance with the concentrations found with LC-MS-MS-QQQ in the same samples. The concentration in the validation samples has previously been determined to 450, 453 and 566 µg/L NDMA with LC-MS-MS-QQQ.

6 Artefact study

6.1 Nitrosation

Nitrosation is the formation of nitrosamines by reaction between amines and nitrogen oxide(s). It is known that secondary amines will undergo chemical reactions with nitrite to form nitrosamines. It is of great importance to prevent that nitrosation occurs within the instruments during analysis and at any point from capture of sample, via transfer, storage and sample preparation to the instrumental analysis.

A major scope of this study has been to ensure that nitrosation does not occur as part of the instrumental analysis. This has been done by series of experiments involving secondary amines and nitrite. In some experiments, sulfamic acid has been tested as scavenger. A main focus has been directed against the quantitative and highly sensitive LC-MS-MS-QQQ methods developed for nitrosamines. The reason for this is that the artefactual formation of even small amounts of nitrosamines theoretically may cause erroneous false positive results with an overestimation of the nitrosamine concentrations.

6.1.1 Quantitative method for nitrosamines

To our knowledge, the LC-MS-MS-QQQ methods are the most sensitive and specific methods for quantitation of nitrosamines. As a main rule, all LC methods that separates analytes with a pKa value (like amines and carboxylic acids) need a mobile phase with a defined pH value to keep the analytes in a controlled state (i.e. charged or uncharged). With LC-MS, it is difficult to use mobile phases that contain non-volatile buffers, like phosphate, because this will result in massive deposition of phosphate within the ion source of the LC-MS system. For this reason, all buffers for LC-MS has been based on volatile buffer constituents like formic acid, ammonium formate and ammonium acetate, or combinations of these. As nitrosation is facilitated by acidic pH, it was important to verify that the mobile phase conditions selected are the safest possible with respect to facilitation of nitrosation during injection or during the chromatographic separation.

To test nitrosation under different conditions, relatively high, but not unrealistic concentrations of secondary amine (10 mM) and nitrite (4 mM) were chosen. The two most frequently used buffer systems used were tested; formic acid (25 mM, pH ca. 2) and ammonium acetate (12.5 mM, pH ca. 7). Under these conditions, it was found that with ammonium acetate, no nitrosation occurred from the corresponding secondary amine that resulted in formation the nitrosamines NDELA, NDMA, NDEA, NPIP, NMOR, NPZ and NDPZ. With formic acid, nitrosation occurred yielding NPZ, DNPZ and NMOR, but not NDMA, NDEA and NPIP. The experiment shows that nitrosation is prone to take place for some nitrosamines under acidic conditions, but for some nitrosamines not. Based upon the finding that no nitrosation was found with ammonium acetate for any of the nitrosamines included in this study, ammonium acetate was chosen as the standard mobile phase buffer constituent for method development in this project.

It should be noted that all nitrosamine methods have been tested both with ammonium acetate and formic acid as mobile phase constituent on different samples. During these tests, it has not been found differences between results from the same sample analyzed with both ammonium

acetate or formic acid as mobile phase constituents. The reason for this is probably that during injection (from injector to the column inlet) there is virtually no contact between the sample and the mobile phase because the sample is transported as a “plug” within the LC tubing. Then, when entering the column, the amine will be retained by the column, while the very water soluble NO_2 will follow the injection front and consequently be removed instantly forward and away from the amine. The very short (if any) contact between amine and NO_2 with formic acid is consistent with no observation of elevated nitrosamine levels in samples analyzed with formic acid in the mobile phase.

With a modern autosampler (autoinjector) there is in fact another way to totally eliminate contact between amine and NO_2 and formic acid in a formic acid based mobile phase system. The autosampler can be programmed to perform injections in a “sandwich” mode where a water plug is placed both in front and behind the sample plug inside the tubing. By performing injections in this mode, the NO_2 will be pushed forward by the water plug behind the sample (while the amine is retained instantly), consequently the amine and the NO_2 will already be well separated before the formic acid mobile phase enters the column behind the last water plug. One reason to consider the sandwich injection principle is that on some LC-MS systems with lower sensitivity than the LC-MS-MS-QQQ system used by SINTEF, a formic acid based mobile system may give a somewhat better sensitivity than an ammonium acetate based mobile phase system due to better ionization (protonization) by the formic acid. Our recommendation is, however, to use the ammonium acetate based mobile phase system described for all nitrosamine methods in Appendix 2.

6.1.2 Screening method for nitrosamines

The GC-MS-NCD screening method for nitrosamines has been tested with respect to nitrosation with piperazine (1.5 M, diluted by a factor of 10 to allow safe injection). The concentration of NO_2 was 4 mM and injections were made from the vial immediately. The experiment showed that no NPZ (below the LOD of 2 mg/L corresponding to 0.017 mM) was formed in the vials. It can be concluded from this experiment that if nitrosation occurs within the vial or within the injector, the amounts of nitrosamine formed are more than 200 times lower than the concentration of NO_2 on a molar basis.

6.1.3 Group method for nitrosamines

Nitrosation is not a concern by instrumental analysis of NO released from nitrosamines with the CuCl / HCl method.

7 Interaction study

Interaction between the compounds within the scope of this study (i.e. the compounds listed in Appendix D in SoW) may appear as result of analytical interactions and/or chemical interactions between compounds that may react chemically with each other.

7.1 Analytical interactions

Analytical interactions may appear either within the chromatographic system or within the mass spectrometer. Chromatographic interactions are typical when a minor compound (i.e. a nitrosamine) is to be analyzed in the presence of a major compound (i.e. a solvent amine). This is an obvious challenge within the scope of this project where concentrations below 1 ug/L of a nitrosamine is to be analyzed in a sample that contain up to 300 g/L of a solvent amine. This range in concentration actually represent up to ten orders of magnitude from low nanomolar up to 5 molar concentrations.

Interactions with the solvent amines and the nitrosamines in this study have been eliminated by development of chromatographic methods that ensures that the nitrosamines will elute before the amines. This concept prevents chromatographic interactions as peak broadening caused by overloading of the column capacity, and mass spectrometric interactions as decreased sensitivity caused by ion suppression when a minor compound is eluted on the back of large solvent peak that elutes first in front of the analyte.

It could also be noted that we have developed a chromatographic system for analysis of DEA where DEA elutes before MEA, which is not the normal elution order for these two compounds. Elution of DEA before MEA is, in analogy with the nitrosamines, very valuable by detection of small amounts of DEA in large amounts of MEA.

It can be concluded that the challenge with possible analytical interactions between the compounds listed in Appendix D in this project has been solved. The two major reasons for this are: 1) the development of chromatographic systems that allows the nitrosamine analytes to be eluted before the solvent amine compounds, and 2) the application of a highly specific and sensitive triplequadrupole mass spectrometric detection principle that allows secure identification and sensitive quantitation.

It should be emphasized that deuterated internal standards should be applied as obligatory part of the analytical method wherever available. The major reason for this is that with a deuterated

internal standard, that normally co-elutes with the analyte, the negative effects from ion suppression is eliminated. In practice this means that potential alterations in response for a given analyte will be corrected for by the interneal standard. In addition, internal standards will in general enhance the accuracy and the precision of the method because any loss or errors during sample preparation will be corrected for.

7.2 Chemical interactions

No indication of chemical interactions between any of the analytes in Appendix D of SoW have been found in this study.

In the VOCC experiment an artificial mix of 14 compounds representing all groups of amine related compounds in Appendix D of SoW was heated and circulated within the VOCC pilot rig. For experimental details, see Appendix 1. During this experiment, no indication of interactions between compounds was observed, and the concentrations found were close to the concentrations expected within the circulating solution.

One compound, however, formamide deviated from the theoretical concentration expected in the study as only about 5% of the expected was found. The reason for this low concentration is not known, but a product information sheet from Sigma states that formamide may react with oxygen and oxidize to formic acid. No major loss of formamide has been detected in the stability studies.

The fact that formamide seems to disappear during the VOCC experiment can not be explained at the present time, and may need a closer investigation. None of the other compounds in the experiment was found to disappear.

8 Stability study

Stability of the nitrosamines (DNPZ, NPZ, NDELA, NDMA, NMOR, NPYR, NMEA, NDEA, NPIP, NMPA and NMBA), the amides (formamide and acetamide) and the aldehydes (formaldehyde and acetaldehyde) was examined experimentally in this study. The stability of the aldehydes was tested as underivatized aldehydes and after derivatization with DNPH (dinitrophenylhydrazine). The stability of all compounds was tested in water. The stability was tested without exposure to light at +50ºC, +20ºC, +4ºC and -20ºC, and with exposure to light at +20ºC. The stability was tested in glass and plastic (high density polyethylene, HDPE)

containers. Stability was tested at two different concentrations in two different studies. In the first study, stability was tested at 2 mg/L (nitrosamines) for a duration of 50 days and 68 days and at 2 g/L (aldehydes and amides) for durations of 48 and 61 days. In the second study, stability was tested at 200 µg/L (nitrosamines) for a duration of 18 days and 2 mg/L (aldehydes and amides) for 34 days and at 200 µg/L (aldehydes and amides) for 21 days.

The results from the stability studies are tabulated in Appendix 4.

The results from the stability studies can be summarized as follows:

Nitrosamines

Nitrosamines are stable in the dark at +50ºC, +20ºC, +4ºC and -20ºC for at least two months. Exposure to light (clear vials) seems to reduce the concentration at long durations. Plastic containers reduce the concentration of NDBA and NDPA considerably, even when the samples are frozen. The rather unpolar characteristics of NDBA and NDPA may explain the loss of these compounds as a result of adsorption to the walls of the containers.

Amides

Formamide is stable under all conditions tested (all temperatures, light and dark, long duration, glass and plastic containers). Acetamide has a reasonably high stability, but not under exposure to light. The results from the high/low and glass/plastic are somewhat contradictory and the loss of formamide in the VOCC study indicates that the stability of the amides should be studied closer in a new study.

Aldehydes

Formaldehyde and acetaldehyde seem stable under all conditions tested at very high concentrations, but stable only at -20ºC at low concentrations. The instability at low concentration is valid both for glass and plastic containers.

Aldehydes after derivatization with DNPH

This study shows clearly that storage temperature strongly affects the concentration of the DNPH-derivative during storage. The study indicates that the derivatization reaction not is complete during the 2 hours period at room temperature before samples were taken to their respective temperature zones for storage. The low concentration of DNPH derivative found after storage at -20ºC, may indicate that the derivatization reaction is reversed by low temperature. From this study, it is not recommended to store the samples as DNPH derivatives, but rather as underivatized aldehydes stored at – 20ºC.

It is recommended to perform new stability studies with real sorbent solutions when new and optimized sorbent systems and solutions have been developed in a second call-off.

9 Validation study

A validation study has been performed with NILU as subcontractor. In the validation study, NILU has analyzed 10 samples from SINTEF. The sample matrix is Aminox wash water provided by Company. The samples are spiked with NDMA, NDELA and NPZ. Five of the samples have been made as parallels to test the reproducibility.

9.1 Sample preparation procedures

9.1.1 General

It is well known that sample preparation may affect the integrity of a sample. This is valid for the nitrosamines due to the problem with nitrosation. Our general strategy has been not to expose the sample to any changes in its chemical environment before the instrumental analysis, except for dilution. This strategy is possible due to the fact that the quantitative LC-MS-MS-QQQ methodology has an analytical sensitivity sufficient to quantify the analytes even after a dilution step.

9.1.2 Flue gas samples

A standardized methodology for simultaneous sampling of all the compounds listed in Appendix D of SoW does not exist. For the solvent amines and the alkylamines, sampling into sorbent solutions consisting of a dilute aqueous solution of an acid (as 0.1 N H_2SO_4) is an obvious candidate, and H_2SO_4 has been applied as sorption solution for basic amines in the literature. The VOCC sampling experiments (Appendix 1) also confirm the functionality of H_2SO_4 as sorbent for amines with respect to sampling efficiency. 0.1 N H_2SO_4 is injectable on LC-MS-MS-QQQ without dilution, however, 0.1 N H_2SO_4 is a sample matrix that may cause problems with respect to the long-term robustness for GC columns. From what is known about nitrosation and the enhancing effects of low pH, 0.1 N H_2SO_4 is not considered as suitable for sampling of nitrosamines if NO_2 is present.

Condensate from a cold trap has been suggested by us as an alternative sampling method. With this sampling method, the resulting sample matrix will consist of water containing only the

analytes that are captured with the water in the cold trap. The results from the VOCC experiment (Appendix 1) are promising with respect to capture of solvent amines, alkylamines and the nitrosamine NDMA. Condensate water is injectable directly without dilutiuon both on LC-MS-MS-QQQ and GC-MS-NCD systems. Unlike 0.1 N H_2SO_4 sorbent solution, the condensate contain no major constituent except for the analytes themselves, therefore a considerable potential exist for concentrating of the condensate sample, and several techniques exist for removing the water. The condensate samples will naturally have a pH value between and 7.5 and 9, depending on the amine solvent system. This range of pH is considered as favourable with respect to prevention of nitrosation.

Validated sampling procedures for flue gas does not exist for many of the analytes in this study. This is valid for the nitrosamines, the amides and the aldehydes, while ammonia, the amines and the alkylamines seem to be trapped adequately by acidic sampling media. (NB: It is emphasized that mass balance studies for sampling from moist flue gas not have been found in the literature for any of these compounds.) For these reasons, no specific sampling procedures has been referred to explicitely in the analytical procedures, but rather as “dilute aqueous absorption solutions” in line with the wash water samples.

9.1.3 Wash water samples

The wash water samples are in many ways comparable with the condensate samples, and what is written above for the condensate samples will apply also for the analysis of wash water. Wash water samples can normally be injected directly on LC-MS-MS-QQQ and GC-MS-NCD instruments without dilution. The pH of wash water will normally be in the range of 8 to 9, but this will depend on the running conditions of water wash. A pH slightly on the basic side is favourable with respect to nitrosation in the wash water sample.

For wash wash water, no specific procedure has been described in the analytical procedures. The reason for this is that we assume that these samples will be taken by at a valve linked to a reservoir or a circulating liquid system. We assume that the sampling procedures will be influenced by local technical solutions at each plant, and therefore factors like representativeness and contamination during sampling will be of a more generalized kind.

9.1.4 Solvent amine samples

The solvent amine samples contain molar concentrations of the solvent amines. For quantitation of the solvent amine itself, we recommend a 1 : 10 000 dilution of the sample before injection on the LC-MS-MS-QQQ instrument.

For quantitation of minor compounds like nitrosamines in the solvent, we recommend a 1 : 100 dilution of the solvent sample. The reason for this is the risk of overloading of the column that may reduce the chromatographic performance and that injections of stronger dilutions will require longer wash-out time between samples.

For the GC-MS-NCD methods, injection of 1 : 10 dilutions of solvent amine represent no problem with PZ / AMP and MEA solvents.

For solvent amines, no specific procedure has been described in the analytical procedures. The reason for this is that we assume that these samples will be taken by at a valve linked to a reservoir or a circulating liquid system. We assume that the sampling procedures will be influenced by local technical solutions at each plant, and therefore factors like representativeness and contamination during sampling will be of a more generalized kind.

9.2 Liquid – liquid extraction procedure for wash water and amine solvent

A liquid – liquid extraction (LLE) procedure has been developed for analysis of nitrosamines in samples that not can be analyzed by dilution, either due to very low nitrosamine concentration or due to analytical interference from amines / amine compounds. The procedure has been developed to avoid exposure of the sample to an acidic environment in order to prevent nitrosation.

A generalized procedure is given below for wash water and amine solvent:

1) The sample (2.5 mL wash water or 250 uL amine solvent) is added deuterated internal standard (50 to 100 µg/L)
2) 3 mL of saturated phosphate buffer is added
3) 9 mL of ethyl acetate extraction solvent is added
4) The mixture is vortexed and centrifuged (10 min at 4000 rpm)
5) The ethyl acetate phase is transferred to a new tube
6) The ethyl acetate phase is evaporated to a volume of ca. 1 mL with nitrogen

7) 100 uL of water is added to the ethy lacetate phase
8) The combined ethyl acetate and water phase is evaporated to ca. 100 uL
9) The 100 uL sample (mainly consisting of water) is transferred to an autosampler vial and capped.
10) The sample is analysed by LC-MS-MS-QQQ or by GC-MS-NCD.

Preparation of phosphate buffer: 15 g KH_2PO_4 and 30 g of Na_2HPO_4 is added to 100 mL of water. The pH of the buffer should be 7.4.

This procedure will reduce the amount of amine in wash water or amine solvent samples.

9.3 Validation – general remarks on reproducibility between laboratiories

Reproducibility (day-to-day variation) measured as %RSD (%CV) will inevitably give larger numerical values than repeatability (instrument variation). Reproducibility should be determined when the matrices of the flue gas sample solutions are known and better defined.

Based upon general experience, both random and systematic error will contribute significantly to a poorer reproducibility when different laboratories are compared. Calculations have been made that have shown that the reproducibility (%RSD) of an in-house method may increase by 40 to 50% when the same method is validated in an interlaboratory test. This numerical value presupposes that the same metodology is being used in the in-house validation as in the interlaboratory test. Also, some pre-assumptions must be stated about the quality of the general quality and performance about the interlaboratory test. The above value is based upon general comparisons, and may only be indicative for amine-related analyses. Since amine-related analyses not have been established at many laboratories over time, one may assume that reproducibility in an interlaboratory test would show even larger differences (poorer reproducibility) in an interlaboratory test than the above 40 to 50 % in an in-house method test.

9.4 Validation – uncertainty budget

Regarding the uncertainty budgets for different samples of amine solvents, wash water and flue gas, there are yet matters to be clarified regarding sample matrices and sample preparation procedures. Based on earlier experience and on work with widely different amine matrices (from dilute aqueous solutions to extensively used amine solvents) it seems clear that the condition of the sample will contribute significantly to the uncertainty of the total budget. As can be seen

from the validation reports, the RSD for reproducibility for most compounds lies well below 5% for the LC methods for nitrosamines and amines. For the GC methods for alkylamines, the RSD normally lies closer to 10%. This most likely reflects the different injection principles of LC and GC methods. We would assume that uncertainty that comes from the matrices and sample treatment for the different matrices would count for as much as 10 to 20 % of the total uncertainty of the analysis. The use of deuterated internal standards will lower the contribution to the uncertainty budget from matrices and sample preparation significantly, and should therefore be applied whenever available.

9.5 Validation – cross validation with NILU

The results from the cross validation with NILU is given in Appendix 5, and summarized in Table 9.5.1 below. The results from NILU comprise the analytes NDMA, NDELA and NPZ. The results from NILU have been analysed with NILUs in-house methodology for nitrosamines, by direct injection without sample preparation.

The results from NILU are consistent with the spiked levels and measurements made by SINTEF. The results for NDELA are very close to the spiked values, the results for NDMA are slightly elevated, and the results for NPZ are somewhat lower than the spiked levels.

Table 9.5.1
Concentrations of nitrosamines NDELA, NDMA and NPz in spiked samples as measured by SINTEF and NILU. Grey, spiked concentrations (from stock solutions); blue, concentrations measured by SINTEF; red. concentrations measured by NILU.

Sample ID	NDELA			NDMA			NPz			Unit
	Spike	SINTEF	NILU	Spike	SINTEF	NILU	Spike	SINTEF	NILU	
Sample A	0	4	< 30	0	< 2,5	**	0	<0,5	< 30	µg/L
Sample B	100	98	99	100	97	143	100	99	71	µg/L
Sample C	200	197	193	200	196	275	200	204	152	µg/L
Sample D	400	395	367	400	396	497	400	415	310	µg/L
Sample E	1000	967	952	1000	984	1294	1000	1044	724	µg/L
Sample F	500	502	473	500	494	640	500	520	367	µg/L
Sample G	500	483	503	500	483	662	500	523	352	µg/L
Sample H	500	481	543	500	486	670	500	523	368	µg/L
Sample I	500	482	505	500	486	623	500	526	359	µg/L
Sample J	500	463	435	500	478	684	500	525	330	µg/L

**Confirming ion not detected for this sample.

Conclusions

The following results have been made:

1) For all 21 compounds listed in the scope of work, methodology has been developed and validated

2) Method descriptions has been made in accordance with ISO 17025

3) Validation reports has been made in accordance with ISO 17025

4) For the nitrosamines, three different types of methods have been made: i) quantitative methods for secure identification and sensitive quantification based on LC-MS-MS-QQQ, ii) screening methods for detection and quantification based on GC-MS-NCD (TEA) detection and iii) a group method giving total amount of nitrosamines based on release of NO (the nitroso group) after treatment with CuCl and HCl in a closed vial followed by subsequent analysis of NO on GC-MS-NCD

5) In an artefact study nitrosation has been studied experimentally and the potential formation of nitrosamines during instrumental analysis has been eliminated

6) An interaction study has been performed to ensure that interaction/interference not occur between the compounds studied

7) A stability study has been performed for nitrosamines, amides and aldehydes

8) Flue gas samples has been made experimentally on the VOCC rig, the flue gas samples have been sampled by three different sampling systems and the results from the samplings are given

9) A cross-validation of quantitative nitrosamine methodology has been made in collaboration with NILU.

10 References

Wang J. et al.: Determination of total N-nitroso compounds by chemical denitrosation using CuCl, J. Agric. Food Chem. 2005, 53, 4686-4691.

11 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
EDA	1,2-Diaminoethane
AMP	2-Amino-2-methyl-1-propanol
MDEA	N-Methyldiethanolam
DNPH	Dinitrophenylhydrazine
BSC	Benzenesulfonylchloride
HDPE	High Density PolyEthylene

APPENDIX 1:
VOCC experiment, procurement of samples, sampling and results

1 Introduction

In order to procure gas samples from a pilot scale plant and to validate methodology for gas sampling and analysis, the VOCC (Validation of CO_2 Capture) test rig was applied for sampling of realistic gas samples.

The VOCC absorption column was operated as a simulated amine scrubber water-wash system in order to facilitate realistic sampling conditions and to validate selected methodology for gas sampling and analysis. A synthetic wash-water containing controlled concentrations of amines, ammonia, aldehydes, amides, alkylamines and nitrosamines was circulated over the column counter-currently with air with 0.5 vol % CO_2 in the closed system. The temperature of the water-saturated gas out of the column was controlled by controlling the temperature of the circulated liquid in order to produce realistic conditions for sampling of wet gas.

This document describes the experimental setup and the developed procedures for the procurement of gas samples from the VOCC test rig.

2 The VOCC test rig

The VOCC test rig was originally built for experimental studies of different packing materials in a 0.5 m diameter CO_2 absorber column. The rig was the experimental basis of the VOCC project (2007-2010) for studies of hydraulic properties like pressure drop, liquid holdup in the packing and mass transfer properties like active area of the packing for a range of different gas- and liquid loads and CO_2 concentrations into the absorber column. The absorber test rig has a total height of 18 m (packing height 5 m) designed for superficial gas velocities up to 5 m/s and a maximum liquid flow of 60 m^3/m^2h. The absorber can be run in batch mode with 2 m^3 of solvent, or in continuous mode with recycling of solvent over the absorber. The lean solvent can be preheated by circulation over a 6 kW electric heater, or cooled by an integrated coil for cooling water in the tank.

The test rig has an adjacent 7 meter tall, well instrumented desorber rig with a 52 kW electric reboiler for the regeneration of amine. Up to 300 kg CO_2 per hour can be added to the gas into the absorber from an outdoor tank of liquid CO_2. This CO_2 supply is built specially for the VOCC test rig and has an integrated 40 kW electric evaporator unit and a setup for pressurising the headspace of the CO_2 tank in order to achieve a stable gas supply.

The absorber column is well instrumented with monitoring of temperature and pressure at every meter of height in the absorber column. The column is also equipped with a special device (designed at SINTEF) for measuring liquid distribution in the column cross-section below the packing, and it has a setup for accurate measurement of liquid hold-up in the packing. CO_2 content of the gas is measured online by IR-analyzers in and out of the absorber column. In addition, a device for online measurement of CO_2 loading and concentration of the amine out of the absorber has been developed in the project by the use of liquid FTIR analysis. Figure 1 shows a process flow diagram (PFD) of the complete VOCC test rig.

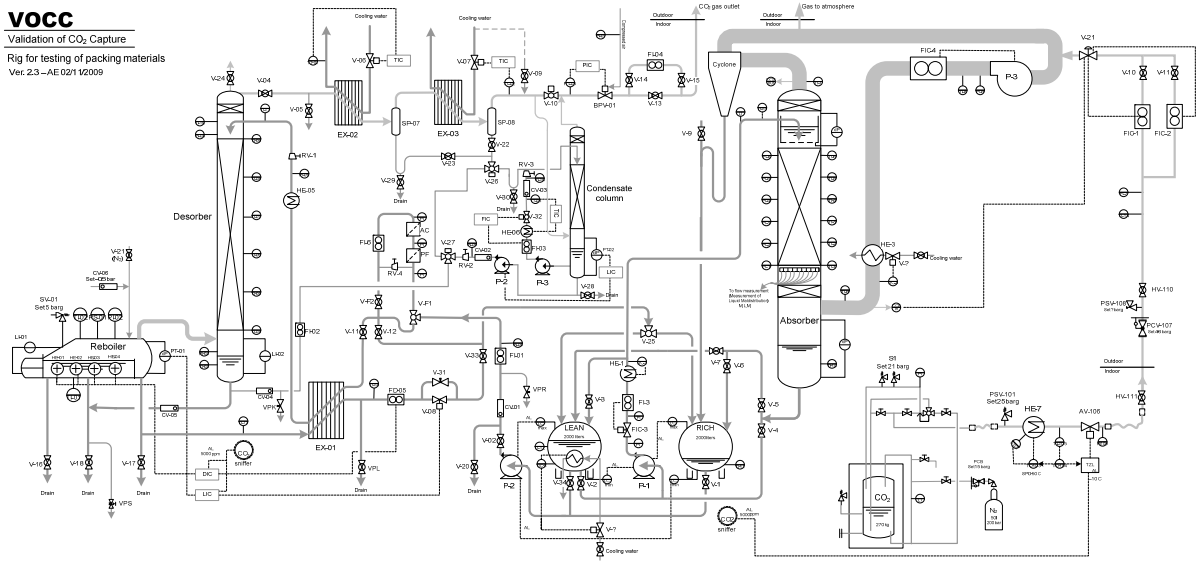

Figure 2.1 Process Flow Diagram of the complete VOCC test rig with absorber and desorber section and CO_2 supply.

3 Experimental procedures

3.1 Gas sampling procedures

3.1.1 Sampling point

The main column of the test rig has an inner diameter of 500 mm with a narrowing of the pipe through a cone down to 300 mm downstream the demister. The sampling point for gas out of the simulated water wash will be located in the 300 mm pipe tangent section downstream the demister of the column, 8 diameters (2.4 m) downstream the pipe fitting of the cone and 2 diameters (0.6 m) upstream the first bend of the straight piping. A superficial gas velocity of 3.0 m/s in the column gives a gas velocity of about 8.3 m/s in the sampling point. In order to minimize condensation of water prior to the sampling point, the 300 mm straight pipe is insulated using a 10 cm thick layer of rock-wool type insulation covered with aluminium foil. The sampling point is located in the 6th floor of the chemistry hall, easily accessible with dedicated workspace for the gas sampling. Figure 2 shows a drawing of the absorber section of the VOCC test rig with the position of gas sampling point used in the described experiments.

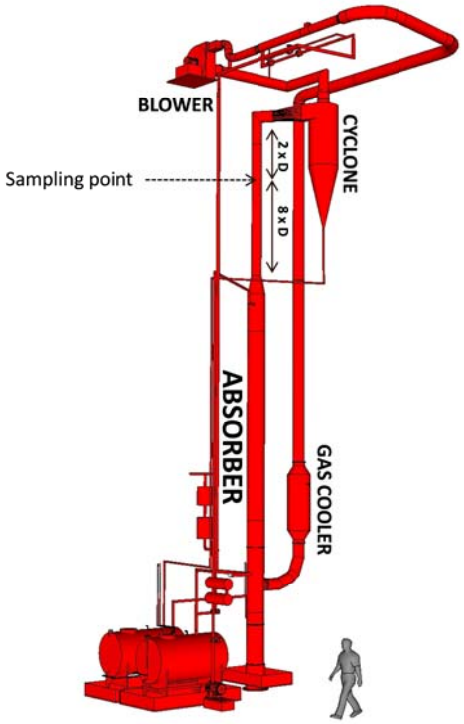

Figure 2 The VOCC test rig at SINTEF Materials and Chemistry in Trondheim. The figure visualizes the absorber section of the test rig with the location of gas sampling point downstream the demister of the column.

3.1.2 Operation of the test rig during procurement of gas samples

The circulation rates of gas and liquid was kept unchanged and the temperature was automatically regulated to 50°C during the gas sampling periods. Liquid flow-rate in the column was 33 litres per minute ($10 m^3/m^2h$ in the column) and superficial gas velocity in the main column was 3.0 m/s (2120 m^3/h). The CO_2 concentration in the gas out of the column was monitored to ensure fully loaded amines in the synthetic wash-water.

3.1.3 Gas sampling methods

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

- **"ISOK 4":** cooled probe and train of gas washing bottles with acidic absorption solution (first bottle empty).
- **"Impinger":** short probe (no cooling) and train of impinger bottles with acidic absorption solution (last bottle empty).
- **"Cold-trap":** collection of condensate in a 2-step condensation, at 2° C and 85° C subsequently.

Exhaust gas from the sample trains was vented over the roof through closed piping. During the sampling period, liquid samples from the column sump was collected periodically over the gas sampling period.

3.1.3.1 ISOK 4

The ISOK 4 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 132841, VDI 20662 and VDI 38683. Iso-kinetic sampling through a water-cooled probe is shown in Figure 3.

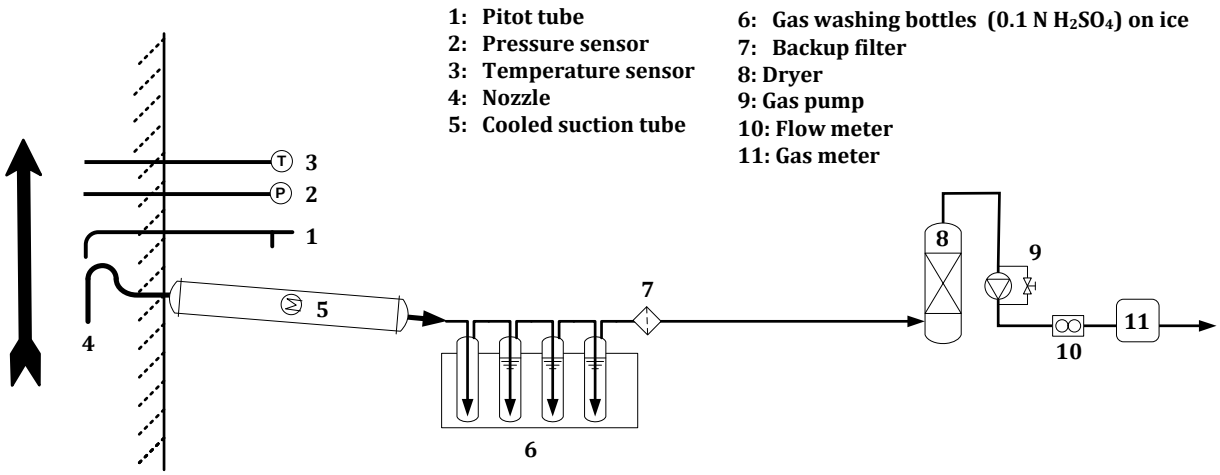

Figure 3 Setup for manual extraction and iso-kinetic sampling of gas samples using the multipurpose system (TSP).

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

[2] VDI 2066-2: Measurement of particulate matter; manual dust measurement in flowing gases; gravimetric determination of dust load; tubular filter devices; VDI 2066-7: Measurement of particulate matter; manual dust measurement in flowing gases; gravimetric determination of dust loads; plane filter devices.

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

The setup will utilize a cooled probe and cooled gas washing bottles positioned in icebath. Note that the first gas washing bottle of the train is empty, thus functioning as a condensate trap.

3.1.3.2 Impinger train

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. This flow is within the optimum operational interval of the 300 ml impingers (optimum operational range 10-16 l/min), thus no splitting of the gas flow was necessary prior to the impinger train. Figure 4 shows the impinger train setup. Note that there is no cooling of the sampled gas prior to the first impinger with 0.1 H_2SO_4.

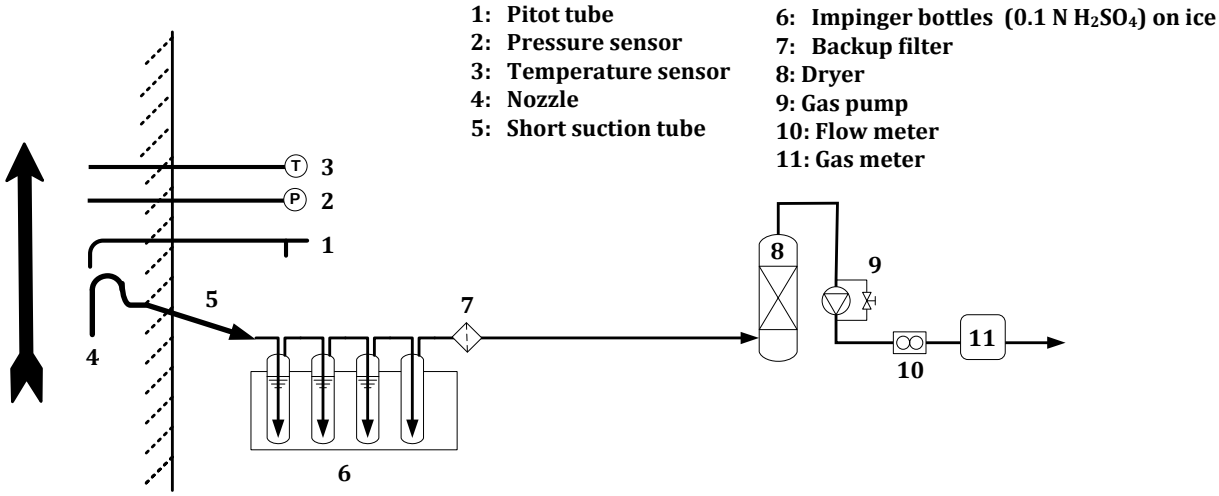

Figure 4 Setup for manual extraction and iso-kinetic sampling of gas samples using an impinger train setup.

3.1.3.3 Collection of condensate

A gas setup of glass gas-coolers was applied for the collection of condensate. The condensator was cooled by the use 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 5 shows the described setup for condensate collection.

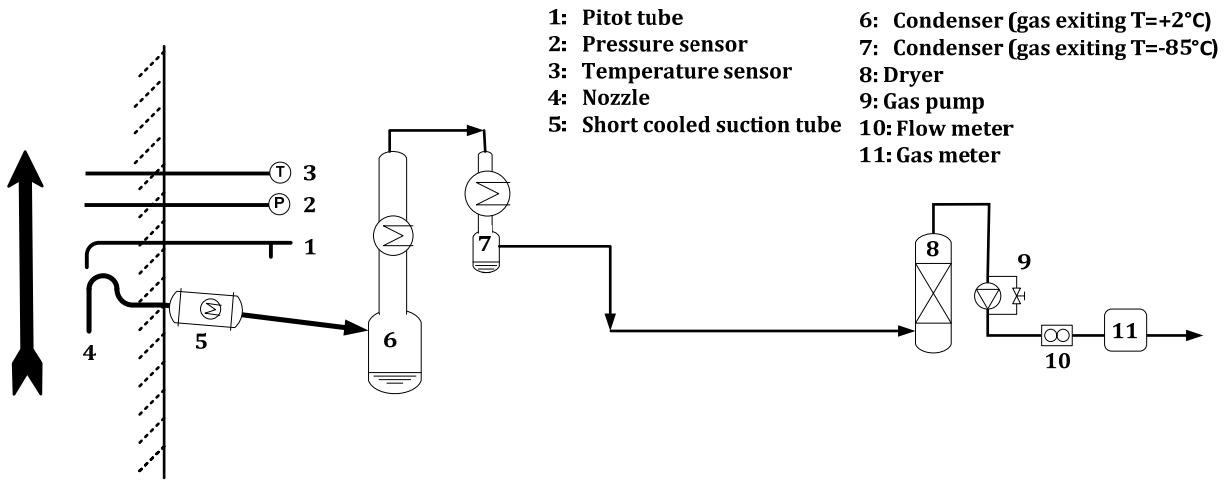

Figure 5 Setup for manual extraction and iso-kinetic sampling of gas samples using two subsequent gas coolers for condensate collection at +2°C and then -85°C.

3.2 Test rig operation

Approximately 170 litres of water was added to the sump of the absorber column and circulated over the column through an electric heater at a rate of 33 litres per minute ($10 m^3/m^2h$ in the column) in order to heat the water to a temperature of 50°C. 2120 m^3/h of air was blown by a fan counter currently over the column in the closed gas loop of the test rig in order to achieve a superficial gas velocity in the main column of 3.0 m/s (and 8.3 m/s at the sampling point in the 300 mm diameter gas channel). CO_2 was added to the gas to a concentration of 0.5 vol% CO_2 during the experiment and concentration of CO_2 was continuously monitored in the out of the absorber.

The test rig was run unmanned over night in order to achieve the correct temperature of the system (it took approximately 5 hours to heat the water to 50°C by this procedure). Condensate produced in the cyclone downstream the column (approx 4 litres condensate pr hour at 50°C out of the column) was collected and pumped back to the sump of the column continuously.

A container of 5 litre cocktail of chemicals was connected to a valve and transferred to the sump of the column through a closed transfer line. A liquid sample was withdrawn from the column sump prior to adding of the chemicals. The rig was run for 1 hour in order to achieve good mixing of the synthetic wash water and the establishment of equilibrium between the liquid and gas phase of the system.

The test rig was then ready for sampling of gas downstream the column. The compounds and concentrations applied for the water circulating over the test rig column are listed on next page:

Compound	Planned concentration	Total amount in 200 L
Amines		
MEA	1 g/L	200 g
Piperazine	1 g/L	200 g
AMP	1 g/L	200 g
Ammonia	10 mg/L	2 g
Aldehydes		
Formaldehyde	1 mg/L	0.2 g
Acetaldehyde	1 mg/L	0.2 g
Amides		
Formamide	1 mg/L	0.2 g
Acetamide	1 mg/L	0.2 g
Alkylamines		
Methylamine	1 mg/L	0.2 g
Ethylamine	1 mg/L	0.2 g
Dimethylamine	1 mg/L	0.2 g
Diethylamine	1 mg/L	0.2 g
Nitrosamines		
NDMA (N-Nitrosodimethylamine)	300 µg/L	60 mg
NDELA (N-Nitrodietanolamine)	300 µg/L	60 mg

Table 1: Concentration of amines (piperazine, MEA and AMP) in liquid samples acquired during the VOCC experiment.

Sample ID	Piperazine	MEA	AMP	Unit
Sump liquid sample, before adding mix to plant 09:21	ND	0,03	0,00	g/L
Sump liquid sample 09:39	1,12	1,15	1,18	g/L
Sump liquid sample 10:03	1,12	1,15	1,19	g/L
Sump liquid sample 10:21	1,11	1,15	1,18	g/L
Sump liquid sample 10:42	1,11	1,15	1,15	g/L
Sump liquid sample 11:15	1,12	1,14	1,16	g/L
Sump liquid sample 12:43	1,11	1,14	1,17	g/L
Sump liquid sample 13:45	1,14	1,16	1,16	g/L
ISOK4 1.Impinger	1,28	4,35	12,39	mg/L
ISOK4 1. Absorption 1.impinger	0,06	0,34	0,82	mg/L
ISOK4 2. Absorption 2.impinger	0,02	0,05	0,02	mg/L
Impinger 1.impinger	1,46	3,85	12,14	mg/L
Impinger 2.impinger	0,08	0,45	0,91	mg/L
Cold-trap, step 1: + 2 C - first outtake	1,56	7,46	13,87	mg/L
Cold-trap, step 1: + 2 C - last outtake	1,91	5,72	14,74	mg/L
Cold-trap, step 2: -85 C	0,69	1,01	3,78	mg/L
Condensate from cyclone 13:05-13:37	44,11	119,07	298,23	mg/L
Sump liquid sample after washing	0,07	0,37	0,19	mg/L
BLIND 0,1N H_2SO_4 used in gas absorption	ND	0,04	ND	mg/L

Table 2: Concentration of nitrosamines (NDELA and NDMA) in liquid samples acquired during the VOCC experiment.

Sample ID	NDELA	NDMA	Unit
Sump liquid sample, before adding mix to plant 09:21	< 1	< 1	µg/L
Sump liquid sample 09:39	356	352	µg/L
Sump liquid sample 10:03	347	349	µg/L
Sump liquid sample 10:21	352	340	µg/L
Sump liquid sample 10:42	353	340	µg/L
Sump liquid sample 11:15	334	334	µg/L
Sump liquid sample 12:43	350	335	µg/L
Sump liquid sample 13:45	345	330	µg/L
ISOK4 1. Impinger	< 1	566	µg/L
ISOK4 1. Absorption 1.impinger	< 1	102	µg/L
ISOK4 2. Absorption 2.impinger	< 1	8	µg/L
Impinger 1.impinger	< 1	453	µg/L
Impinger 2.impinger	< 1	251	µg/L
Cold-trap, step 1: + 2 C - first outtake	< 1	450	µg/L
Cold-trap, step 1: + 2 C - last outtake	< 1	527	µg/L
Cold-trap, step 2: -85 C	< 1	207	µg/L
Condensate from cyclone 13:05-13:37	< 1	317	µg/L
Sump liquid sample after washing	< 1		µg/L
BLIND 0,1N H_2SO_4 used in gas absorption	< 1	< 1	µg/L

Table 3: Concentration of amides (formamide and acetamide) in liquid samples acquired during the VOCC experiment.

Sample ID	Formamide	Acetamide	Unit
Sump liquid sample, before adding mix to plant 09:21	ND	ND	µg/L
Sump liquid sample 09:39	48	1051	µg/L
Sump liquid sample 10:03	52	1055	µg/L
Sump liquid sample 10:21	49	1040	µg/L
Sump liquid sample 10:42	49	1048	µg/L
Sump liquid sample 11:15	54	1033	µg/L
Sump liquid sample 12:43	64	1032	µg/L
Sump liquid sample 13:45	69	1028	µg/L
ISOK4 1. Impinger	< 10	< 10	µg/L
ISOK4 1. Absorption 1.impinger	< 10	< 10	µg/L
ISOK4 2. Absorption 2.impinger	< 10	< 10	µg/L
Impinger 1.impinger	11	18	µg/L
Impinger 2.impinger	0	< 10	µg/L
Cold-trap, step 1: + 2 C - first outtake	118	< 10	µg/L
Cold-trap, step 1: + 2 C - last outtake	25	11	µg/L
Cold-trap, step 2: -85 C	< 10	< 10	µg/L
Condensate from cyclone 13:05-13:37	217	179	µg/L
Sump liquid sample after washing	< 10	< 10	µg/L
BLIND 0,1N H_2SO_4 used in gas absorption	< 10	< 10	µg/L

Table 4: 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	NH_3	Methyl-amine	Ethyl-amine	Dimethyl-amine	Diethyl-amine
Unit	µg/Nm³	µg/Nm³	µg/Nm³	µg/Nm³	µg/Nm³	mg /Nm³	µg/Nm³	µg/Nm³	µg/Nm³	µg/Nm³
ISOK4 - 1.Condensation step (gas absorption bottle without diffuser on water/dry ice)	41,2	None	93,04	317	901,2	8,00	35,144	45,8	48,594	70,781
ISOK4 - 1.Absorption (Gas washing bottle) - 0.1 N H2SO4	9,69	None	5,319	32,6	78,25	7,43	2,92	3,9	3,49	5,44
ISOK4 - 2.Absorption (Gas washing bottle) - 0.1 N H2SO4	0,64	None	1,189	4,07	1,64	ND	1,00	ND	0,57	0,188
ISOK4 - 3. Absorption (Gas washing bottle) - empty										
Impinger train, 1.Absorption impinger - 0.1 N H2SO4	39,2	None	126,6	333	1052	15,67	42,52	54,7	59,23	85,85
Impinger train, 2.Absorption impinger - 0.1 N H2SO4	13,3	None	4,24	23,6	48,31	0,419	2,869	3,82	3,81	4,208
Impinger train, 3.Absorption impinger – empty										
Cold-trap, step 1: + 2 C - first outtake										
Cold-trap, step 1: + 2 C - last outtake	39,5	None	147,8	452	1148	10,08	43,509	53,3	59,19	79,24
Cold-trap, step 2: -85 C	1,35	None	4,459	6,59	24,58	0,139	0,151	0,4	0,481	1,366

APPENDIX 2:

Method descriptions

METHOD DESCRIPTION N-NITROSODIMEHTYLAMINE (NDMA) BY LC-MS-MS-QQQ

APPROPRIATE IDENTIFICATION
NDMA can be detected and identified by liquid chromatography combined with mass spectrometry (LC-MS).

SCOPE
Amine solvents, wash water and flue gas samples.

DESCRIPTION OF SAMPLES
NDMA is a nitrosamine. Wash water is a dilute aqueous solution that may contain NDMA. Flue gas samples may be dilute aqueous absorption solutions of varying composition, including acids, bases or other constituents in significant amounts.

CONCENTRATION RANGES TO BE DETERMINED
The calibration range may cover a range from 2.5 to 5 000 µg/L. If the concentration of NDMA in the sample is higher, the sample should be diluted to a final concentration within the range given above.

INSTRUMENTATION / EQUIPMENT
An Agilent 1290/6460 liquid chromatography – triple quadrupole mass spectrometer (LC-MS-MS-QQQ) system may be used.

Chromatographic conditions:
Column: Discovery HS-F5, (15cm x 2.1 mm, 3 µm)
Mobile phase: 12mM AmAc/MeOH – 50/50
Flow: 0.2 mL/min
Injection volume: 10 µL
Retention time NDMA: ca. 2.71 min

Mass spectrometric conditions:
Ionization: Atmospheric-pressure chemical ionization (APCI), Positive ion mode
Transition: m/z $(M+H)^+$ 75.0 → 43.0 and 75.0 → 58.1

REFERENCE STANDARDS AND REFERENCE MATERIALS
NDMA (N,N-dimethylnitrosamine, N-nitrosodimethylamine, $N(CH_3)_2$-NO, CAS No. 62-75-9, Mw 74.08 g/mol) (>99.5%)
d6-NDMA (deuterated NDMA), CAS No 17829-05-9, Mw 80,12 g/mol (>98% D atom).

ENVIRONMENTAL CONDITIONS / STABILIZATION
Ambient conditions for operation, temperature: 15 to 35ºC, humidity 20 to 80% RH.

PROCEDURES
Samples should be contained in plastic (HDPE) containers. The containers should be stored dark at a low temperature (+4ºC). Shipment of samples with courier (2 days) at ambient temperature is acceptable. Before analysis, the samples should be diluted (if necessary) and transferred to autosampler vials and capped with a crimp-on cap. The autosampler should be refrigerated. Calibration samples should always be analyzed together with the unknown

samples in the same analytical series. For control of analytical performance in large sample series, quality control (QC) samples should be included within the analytical series. The QC samples should be spiked with appropriate concentrations of NDMA within the calibration range. Method data (instrument parameters) should be stored routinely together with the sample data to verify the methodology used for analysis. Data (sample data and method parameters) should be collected and stored also on a back-up file.

The concentration of NDMA in amine solvent should be measured in dilutions of amine solvent diluted to 1:100. Wash water is a dilute aqueous solution that may contain NDMA. NDMA in wash water can be measured by direct injection of the wash water sample. As a main rule, flue gas absorption solutions may also be analyzed by direct injection, however, dilution may be necessary if the absorption solution contains acids, bases or other constituents in significant amounts.

CRITERIA FOR ACCEPTANCE

Acceptance criteria should be applied to chromatographic performance, mass spectrometric performance and the results of the QC samples. Chromatographic criteria: Peak shape should be symmetrical and similar to a calibration standard with comparable concentration, the retention time should be within +/- 2% of the retention time of calibration standard. Mass spectrometric analysis: NDMA has two transitions, and consequently, ion ratio criteria (within +/- 20%) between two signals can be compared.

DATA TO BE RECORDED / METHOD OF ANALYSIS / DATA PRESENTATION

Raw data must be recorded as separate data files. A logic file name structure should be applied to the samples that make it easy and safe to identify analytical series (all the samples analyzed within the same series, together with calibrators and QC samples) as well as the individual unknown samples. Method parameters should be recorded together with raw data, this is normally handled automatically by the instrument software. This is obligatory to secure methodological traceability. It is recommended to calculate concentrations of analyte in unknown samples and QC samples as a batch process. This will allow for more efficient data handling.

UNCERTAINTY OF PROCEDURE

The relative uncertainties of the different steps of the methodological procedure should be estimated and tabulated as an uncertainty budget. The overall instrumental precision measured as % RSD (Relative Standard Deviation) is better than 7% (n=5) within the measuring range given above.

METHOD DESCRIPTION N-NITROSODIETHYLAMINE (NDEA) BY LC-MS-MS-QQQ

APPROPRIATE IDENTIFICATION
NDEA can be detected and identified by liquid chromatography combined with mass spectrometry (LC-MS).

SCOPE
Amine solvents, wash water and flue gas samples.

DESCRIPTION OF SAMPLES
NDEA is a nitrosamine. Wash water is a dilute aqueous solution that may contain NDEA. Flue gas samples may be dilute aqueous absorption solutions of varying composition, including acids, bases or other constituents in significant amounts.

CONCENTRATION RANGES TO BE DETERMINED
The calibration range may cover a range from 1 to 10 000 µg/L. If the concentration of NDEA in the sample is higher, the sample should be diluted to a final concentration within the range given above.

INSTRUMENTATION / EQUIPMENT
An Agilent 1290/6460 liquid chromatography – triple quadrupole mass spectrometer (LC-MS-MS-QQQ) system may be used.

Chromatographic conditions:
Column: Discovery HS-F5, (15cm x 2.1 mm, 3 µm)
Mobile phase: 12mM AmAc/MeOH – 55/45
Flow: 0.2 mL/min
Injection volume: 10 µL
Retention time NDEA: ca. 4.56 min

Mass spectrometric conditions:
Ionization: Atmospheric-pressure chemical ionization (APCI), Positive ion mode
Transition: m/z $(M+H)^+$ 103.1 → 75.0

REFERENCE STANDARDS AND REFERENCE MATERIALS
NDEA (N,N-diethylnitrosamine, N-nitrosodimethylamine, $N(C_2H_5)_2$-NO, CAS No. 55-18-5, Mw 102.135 g/mol)

ENVIRONMENTAL CONDITIONS / STABILIZATION
Ambient conditions for operation, temperature: 15 to 35ºC, humidity 20 to 80% RH.

PROCEDURES
Samples should be contained in plastic (HDPE) containers. The containers should be stored dark at a low temperature (+4ºC). Shipment of samples with courier (2 days) at ambient temperature is acceptable. Before analysis, the samples should be diluted (if necessary) and transferred to autosampler vials and capped with a crimp-on cap. The autosampler should be refrigerated. Calibration samples should always be analyzed together with the unknown samples in the same analytical series. For control of analytical performance in large sample

series, quality control (QC) samples should be included within the analytical series. The QC samples should be spiked with appropriate concentrations of NDEA within the calibration range. Method data (instrument parameters) should be stored routinely together with the sample data to verify the methodology used for analysis. Data (sample data and method parameters) should be collected and stored also on a back-up file.

The concentration of NDEA in amine solvent should be measured in dilutions of amine solvent diluted to 1:100. Wash water is a dilute aqueous solution that may contain NDEA. NDEA in wash water can be measured by direct injection of the wash water sample. As a main rule, flue gas absorption solutions may also be analyzed by direct injection, however, dilution may be necessary if the absorption solution contains acids, bases or other constituents in significant amounts.

CRITERIA FOR ACCEPTANCE

Acceptance criteria should be applied to chromatographic performance, mass spectrometric performance and the results of the QC samples. Chromatographic criteria: Peak shape should be symmetrical and similar to a calibration standard with comparable concentration, the retention time should be within +/- 2% of the retention time of calibration standard. Mass spectrometric analysis: Due to its low molecular weight, NDEA has only one transition, and consequently, no ion ratio criteria (within +/- 20%) between two signals can be compared.

DATA TO BE RECORDED / METHOD OF ANALYSIS / DATA PRESENTATION

Raw data must be recorded as separate data files. A logic file name structure should be applied to the samples that makes it easy and safe to identify analytical series (all the samples analyzed within the same series, together with calibrators and QC samples) as well as the individual unknown samples. Method parameters should be recorded together with raw data, this is normally handled automatically by the instrument software. This is obligatory to secure methodological traceability. It is recommended to calculate concentrations of analyte in unknown samples and QC samples as a batch process. This will allow for more efficient data handling.

UNCERTAINTY OF PROCEDURE

The relative uncertainties of the different steps of the methodological procedure should be estimated and tabulated as an uncertainty budget. The overall instrumental precision measured as % RSD (Relative Standard Deviation) is better than 3% (n=5) within the measuring range given above.

METHOD DESCRIPTION N-NITROSOMORPHOLINE (NMOR) BY LC-MS-MS-QQQ

APPROPRIATE IDENTIFICATION
NMOR can be detected and identified by liquid chromatography combined with mass spectrometry (LC-MS).

SCOPE
Amine solvents, wash water and flue gas samples.

DESCRIPTION OF SAMPLES
NMOR is a nitrosamine. Wash water is a dilute aqueous solution that may contain NMOR. Flue gas samples may be dilute aqueous absorption solutions of varying composition, including acids, bases or other constituents in significant amounts.

CONCENTRATION RANGES TO BE DETERMINED
The calibration range may cover a range from 10 to 10 000 µg/L. If the concentration of NMOR in the sample is higher, the sample should be diluted to a final concentration within the range given above.

INSTRUMENTATION / EQUIPMENT
An Agilent 1290/6460 liquid chromatography – triple quadrupole mass spectrometer (LC-MS-MS-QQQ) system may be used.

Chromatographic conditions:
Column: Discovery HS-F5, (15cm x 2.1 mm, 3 µm)
Mobile phase: 12mM AmAc/MeOH – 55/45
Flow: 0.2 mL/min
Injection volume: 10 µL
Retention time NMOR: ca. 2.98 min

Mass spectrometric conditions:
Ionization: Atmospheric-pressure chemical ionization (APCI), Positive ion mode
Transition: m/z $(M+H)^+$ 117.1 → 45.0 and 117.1 → 86.0

REFERENCE STANDARDS AND REFERENCE MATERIALS
NMOR (4-nitrosomorpholine, N-nitrosomorpholine, C_4ON-NO, CAS No. 59-89-2, Mw 116.12 g/mol)

ENVIRONMENTAL CONDITIONS / STABILIZATION
Ambient conditions for operation, temperature: 15 to 35ºC, humidity 20 to 80% RH.

PROCEDURES
Samples should be contained in plastic (HDPE) containers. The containers should be stored dark at a low temperature (+4ºC). Shipment of samples with courier (2 days) at ambient temperature is acceptable. Before analysis, the samples should be diluted (if necessary) and transferred to autosampler vials and capped with a crimp-on cap. The autosampler should be refrigerated. Calibration samples should always be analyzed together with the unknown samples in the same analytical series. For control of analytical performance in large sample

series, quality control (QC) samples should be included within the analytical series. The QC samples should be spiked with appropriate concentrations of NMOR within the calibration range. Method data (instrument parameters) should be stored routinely together with the sample data to verify the methodology used for analysis. Data (sample data and method parameters) should be collected and stored also on a back-up file.

The concentration of NMOR in amine solvent should be measured in dilutions of amine solvent diluted to 1:100. Wash water is a dilute aqueous solution that may contain NMOR. NMOR in wash water can be measured by direct injection of the wash water sample. As a main rule, flue gas absorption solutions may also be analyzed by direct injection, however, dilution may be necessary if the absorption solution contains acids, bases or other constituents in significant amounts.

CRITERIA FOR ACCEPTANCE

Acceptance criteria should be applied to chromatographic performance, mass spectrometric performance and the results of the QC samples. Chromatographic criteria: Peak shape should be symmetric and similar to a calibration standard with comparable concentration, the retention time should be within +/- 2% of the retention time of calibration standard. Mass spectrometric analysis: NMOR has two transitions, and consequently, the ion ratio criteria (within +/- 20%) between two signals can be compared.

DATA TO BE RECORDED / METHOD OF ANALYSIS / DATA PRESENTATION

Raw data must be recorded as separate data files. A logic file name structure should be applied to the samples which make it easy and safe to identify analytical series (all the samples analyzed within the same series, together with calibrators and QC samples) as well as the individual unknown samples. Method parameters should be recorded together with raw data, this is normally handled automatically by the instrument software. This is obligatory to secure methodological traceability. It is recommended to calculate concentrations of analyte in unknown samples and QC samples as a batch process. This will allow for more efficient data handling.

UNCERTAINTY OF PROCEDURE

The relative uncertainties of the different steps of the methodological procedure should be estimated and tabulated as an uncertainty budget. The overall instrumental precision measured as % RSD (Relative Standard Deviation) is better than 3% (n=5) within the measuring range given above.

METHOD DESCRIPTION N-NITROSOPIPERIDINE (NPIP) BY LC-MS-MS-QQQ

APPROPRIATE IDENTIFICATION
NPIP can be detected and identified by liquid chromatography combined with mass spectrometry (LC-MS).

SCOPE
Amine solvents, wash water and flue gas samples.

DESCRIPTION OF SAMPLES
NPIP is a nitrosamine. Wash water is a dilute aqueous solution that may contain NPIP. Flue gas samples may be dilute aqueous absorption solutions of varying composition, including acids, bases or other constituents in significant amounts.

CONCENTRATION RANGES TO BE DETERMINED
The calibration range may cover a range from 0,5 to 10 000 µg/L. If the concentration of NPIP in the sample is higher, the sample should be diluted to a final concentration within the range given above.

INSTRUMENTATION / EQUIPMENT
An Agilent 1290/6460 liquid chromatography – triple quadrupole mass spectrometer (LC-MS-MS-QQQ) system may be used.

Chromatographic conditions:
Column: Discovery HS-F5, (15cm x 2.1 mm, 3 µm)
Mobile phase: 12mM AmAc/MeOH – 55/45
Flow: 0.2 mL/min
Injection volume: 10 µL
Retention time NPIP: ca. 4.80 min

Mass spectrometric conditions:
Ionization: Atmospheric-pressure chemical ionization (APCI), Positive ion mode
Transition: m/z $(M+H)^+$ 115.1 → 41.1 and 115.1 → 69.1

REFERENCE STANDARDS AND REFERENCE MATERIALS
NPIP (1-nitrosopiperidine, N-nitrosopiperidine, C_5N-NO, CAS No. 100-75-4, Mw 114.15 g/mol)

ENVIRONMENTAL CONDITIONS / STABILIZATION
Ambient conditions for operation, temperature: 15 to 35ºC, humidity 20 to 80% RH.

PROCEDURES
Samples should be contained in plastic (HDPE) containers. The containers should be stored dark at a low temperature (+4ºC). Shipment of samples with courier (2 days) at ambient temperature is acceptable. Before analysis, the samples should be diluted (if necessary) and transferred to autosampler vials and capped with a crimp-on cap. The autosampler should be refrigerated. Calibration samples should always be analyzed together with the unknown samples in the same analytical series. For control of analytical performance in large sample

series, quality control (QC) samples should be included within the analytical series. The QC samples should be spiked with appropriate concentrations of NPIP within the calibration range. Method data (instrument parameters) should be stored routinely together with the sample data to verify the methodology used for analysis. Data (sample data and method parameters) should be collected and stored also on a back-up file.

The concentration of NPIP in amine solvent should be measured in dilutions of amine solvent diluted to 1:100. Wash water is a dilute aqueous solution that may contain NPIP. NPIP in wash water can be measured by direct injection of the wash water sample. As a main rule, flue gas absorption solutions may also be analyzed by direct injection, however, dilution may be necessary if the absorption solution contains acids, bases or other constituents in significant amounts.

CRITERIA FOR ACCEPTANCE

Acceptance criteria should be applied to chromatographic performance, mass spectrometric performance and the results of the QC samples. Chromatographic criteria: Peak shape should be symmetric and similar to a calibration standard with comparable concentration, the retention time should be within +/- 2% of the retention time of calibration standard. Mass spectrometric analysis: NPIP has two transitions, and consequently, the ion ratio criteria (within +/- 20%) between two signals can be compared.

DATA TO BE RECORDED / METHOD OF ANALYSIS / DATA PRESENTATION

Raw data must be recorded as separate data files. A logic file name structure should be applied to the samples which make it easy and safe to identify analytical series (all the samples analyzed within the same series, together with calibrators and QC samples) as well as the individual unknown samples. Method parameters should be recorded together with raw data, this is normally handled automatically by the instrument software. This is obligatory to secure methodological traceability. It is recommended to calculate concentrations of analyte in unknown samples and QC samples as a batch process. This will allow for more efficient data handling.

UNCERTAINTY OF PROCEDURE

The relative uncertainties of the different steps of the methodological procedure should be estimated and tabulated as an uncertainty budget. The overall instrumental precision measured as % RSD (Relative Standard Deviation) is better than 3% (n=5) within the measuring range given above.

METHOD DESCRIPTION N-NITROSODIETHANOLAMINE (NDELA) BY LC-MS-MS-QQQ

APPROPRIATE IDENTIFICATION
NDELA can be detected and identified by liquid chromatography combined with mass spectrometry (LC-MS).

SCOPE
Amine solvents, wash water and flue gas samples.

DESCRIPTION OF SAMPLES
NDELA is a nitrosamine. Wash water is a dilute aqueous solution that may contain NDELA. Flue gas samples may be dilute aqueous absorption solutions of varying composition, including acids, bases or other constituents in significant amounts.

CONCENTRATION RANGES TO BE DETERMINED
The calibration range may cover a range from 0.5 µg/L to 5 000 µg/L. If the concentration of NDELA in the sample is higher, the sample should be diluted to a final concentration within the range given above.

INSTRUMENTATION / EQUIPMENT
An Agilent 1290/6460 liquid chromatography – triple quadrupole mass spectrometer (LC-MS-MS-QQQ) system may be used.

Chromatographic conditions:
Column: Discovery HS-F5, (15cm x 2.1 mm, 3 µm)
Mobile phase: 12mM AmAc/MeOH – 50/50
Flow: 0.2 mL/min
Injection volume: 10 µL
Retention time NDELA: ca. 2.27 min

Mass spectrometric conditions:
Ionization: Atmospheric-pressure chemical ionization (APCI), Positive ion mode
Transition: m/z $(M+H)^+$ 135.1 → 74.1 and 135.1 → 104.1

REFERENCE STANDARDS AND REFERENCE MATERIALS
NDELA (diethanolnitrosamine, N-nitrosodiethanolamine, OH-CH_2-CH_2-N(NO)-CH_2-CH_2-OH, CAS No. 1116-54-7, Mw 134.13 g/mol) (>99.5%),
d8-NDELA (deuterated NDELA), Mw 142.18 g/mol (>98% D atom).

ENVIRONMENTAL CONDITIONS / STABILIZATION
Ambient conditions for operation, temperature: 15 to 35ºC, humidity 20 to 80% RH.

PROCEDURES
Samples should be contained in plastic (HDPE) containers. The containers should be stored dark at a low temperature (+4ºC). Shipment of samples with courier (2 days) at ambient temperature is acceptable. Before analysis, the samples should be diluted (if necessary) and transferred to autosampler vials and capped with a crimp-on cap. The autosampler should be refrigerated. Calibration samples should always be analyzed together with the unknown

samples in the same analytical series. For control of analytical performance in large sample series, quality control (QC) samples should be included within the analytical series. The QC samples should be spiked with appropriate concentrations of NDELA within the calibration range. Method data (instrument parameters) should be stored routinely together with the sample data to verify the methodology used for analysis. Data (sample data and method parameters) should be collected and stored also on a back-up file.

The concentration of NDELA in amine solvent should be measured in dilutions of amine solvent diluted to 1:100. Wash water is a dilute aqueous solution that may contain NDELA. NDELA in wash water can be measured by direct injection of the wash water sample. As a main rule, flue gas absorption solutions may also be analyzed by direct injection, however, dilution may be necessary if the absorption solution contains acids, bases or other constituents in significant amounts.

CRITERIA FOR ACCEPTANCE

Acceptance criteria should be applied to chromatographic performance, mass spectrometric performance and the results of the QC samples. Chromatographic criteria: Peak shape should be symmetric and similar to a calibration standard with comparable concentration, the retention time should be within +/- 2% of the retention time of calibration standard. Mass spectrometric analysis: NDELA has two transitions, and consequently, the ion ratio criteria (within +/- 20%) between two signals can be compared.

DATA TO BE RECORDED / METHOD OF ANALYSIS / DATA PRESENTATION

Raw data must be recorded as separate data files. A logic file name structure should be applied to the samples which make it easy and safe to identify analytical series (all the samples analyzed within the same series, together with calibrators and QC samples) as well as the individual unknown samples. Method parameters should be recorded together with raw data, this is normally handled automatically by the instrument software. This is obligatory to secure methodological traceability. It is recommended to calculate concentrations of analyte in unknown samples and QC samples as a batch process. This will allow for more efficient data handling.

UNCERTAINTY OF PROCEDURE

The relative uncertainties of the different steps of the methodological procedure should be estimated and tabulated as an uncertainty budget. The overall instrumental precision measured as % RSD (Relative Standard Deviation) is better than 3% (n=5) within the measuring range given above.

METHOD DESCRIPTION N-NITROSOPIPERAZINE (NPZ) BY LC-MS-MS-QQQ

APPROPRIATE IDENTIFICATION
NPZ can be detected and identified by liquid chromatography combined with mass spectrometry (LC-MS).

SCOPE
Amine solvents, wash water and flue gas samples.

DESCRIPTION OF SAMPLES
NPZ is a nitrosamine. Wash water is a dilute aqueous solution that may contain NPZ. Flue gas samples may be dilute aqueous absorption solutions of varying composition, including acids, bases or other constituents in significant amounts.

CONCENTRATION RANGES TO BE DETERMINED
The calibration range may cover a range from 0.5 µg/L to 5 000 µg/L. If the concentration of NPZ in the sample is higher, the sample should be diluted to a final concentration within the range given above.

INSTRUMENTATION / EQUIPMENT
An Agilent 1290/6460 liquid chromatography – triple quadrupole mass spectrometer (LC-MS-MS-QQQ) system may be used.

Chromatographic conditions:
Column: Discovery HS-F5, (15cm x 2.1 mm, 3 µm)
Mobile phase: 12mM AmAc/MeOH – 50/50
Flow: 0.2 mL/min
Injection volume: 10 µL
Retention time NPZ: ca. 3.09 min

Mass spectrometric conditions:
Ionization: Atmospheric-pressure chemical ionization (APCI), Positive ion mode
Transition: m/z $(M+H)^+$ 116.1 → 86.0 and 116.1 → 44.0

REFERENCE STANDARDS AND REFERENCE MATERIALS
NPZ (1-nitrosopiperazine, N-nitrosopiperazine, $C_4H_5N_2$-NO, CAS No. 5632-47-3, Mw 115.13 g/mol) (>99.5%)

ENVIRONMENTAL CONDITIONS / STABILIZATION
Ambient conditions for operation, temperature: 15 to 35ºC, humidity 20 to 80% RH.

PROCEDURES
Samples should be contained in plastic (HDPE) containers. The containers should be stored dark at a low temperature (+4ºC). Shipment of samples with courier (2 days) at ambient temperature is acceptable. Before analysis, the samples should be diluted (if necessary) and transferred to autosampler vials and capped with a crimp-on cap. The autosampler should be refrigerated. Calibration samples should always be analyzed together with the unknown samples in the same analytical series. For control of analytical performance in large sample

series, quality control (QC) samples should be included within the analytical series. The QC samples should be spiked with appropriate concentrations of NPZ within the calibration range. Method data (instrument parameters) should be stored routinely together with the sample data to verify the methodology used for analysis. Data (sample data and method parameters) should be collected and stored also on a back-up file.

The concentration of NPZ in amine solvent should be measured in dilutions of amine solvent diluted to 1:100. Wash water is a dilute aqueous solution that may contain NPZ. NPZ in wash water can be measured by direct injection of the wash water sample. As a main rule, flue gas absorption solutions may also be analyzed by direct injection, however, dilution may be necessary if the absorption solution contains acids, bases or other constituents in significant amounts.

CRITERIA FOR ACCEPTANCE

Acceptance criteria should be applied to chromatographic performance, mass spectrometric performance and the results of the QC samples. Chromatographic criteria: Peak shape should be symmetric and similar to a calibration standard with comparable concentration, the retention time should be within +/- 2% of the retention time of calibration standard. Mass spectrometric analysis: NPZ has two transitions, and consequently, the ion ratio criteria (within +/- 20%) between two signals can be compared.

DATA TO BE RECORDED / METHOD OF ANALYSIS / DATA PRESENTATION

Raw data must be recorded as separate data files. A logic file name structure should be applied to the samples which make it easy and safe to identify analytical series (all the samples analyzed within the same series, together with calibrators and QC samples) as well as the individual unknown samples. Method parameters should be recorded together with raw data, this is normally handled automatically by the instrument software. This is obligatory to secure methodological traceability. It is recommended to calculate concentrations of analyte in unknown samples and QC samples as a batch process. This will allow for more efficient data handling.

UNCERTAINTY OF PROCEDURE

The relative uncertainties of the different steps of the methodological procedure should be estimated and tabulated as an uncertainty budget. The overall instrumental precision measured as % RSD (Relative Standard Deviation) is better than 3% (n=5) within the measuring range given above.

METHOD DESCRIPTION 1,4-DINITROSOPIPERAZINE (DNPZ) BY LC-MS-MS-QQQ

APPROPRIATE IDENTIFICATION
DNPZ can be detected and identified by liquid chromatography combined with mass spectrometry (LC-MS).

SCOPE
Amine solvents, wash water and flue gas samples.

DESCRIPTION OF SAMPLES
DNPZ is a nitrosamine. Wash water is a dilute aqueous solution that may contain DNPZ and degradation products of DNPZ. Flue gas samples may be dilute aqueous absorption solutions of varying composition, including acids, bases or other constituents in significant amounts.

CONCENTRATION RANGES TO BE DETERMINED
The calibration range may cover a range from 5 to 10 000 µg/L. If the concentration of DNPZ in the sample is higher, the sample should be diluted to a final concentration within the range given above.

INSTRUMENTATION / EQUIPMENT
An Agilent 1290/6460 liquid chromatography – triple quadrupole mass spectrometer (LC-MS-MS-QQQ) system may be used.

Chromatographic conditions:
Column: Discovery HS-F5, (15cm x 2.1 mm, 3 µm)
Mobile phase: 12mM AmAc/MeOH – 50/50
Flow: 0.2 mL/min
Injection volume: 10 µL
Retention time DNPZ: ca. 2.67 min

Mass spectrometric conditions:
Ionization: Agilent Jet Stream (AJS) Electrospray ionization (ESI), Positive ion mode
Transition: m/z $(M+H)^+$ 145.1 → 56.1 and 145.1 → 115.1

REFERENCE STANDARDS AND REFERENCE MATERIALS
DNPZ (1,2-dinitrosopiperazine, $C_4H_4N_2$-$(NO)_2$, CAS No. 140-79-4, Mw 144.13 g/mol) (>99.8%)

ENVIRONMENTAL CONDITIONS / STABILIZATION
Ambient conditions for operation, temperature: 15 to 35ºC, humidity 20 to 80% RH.

PROCEDURES
Samples should be contained in plastic (HDPE) containers. The containers should be stored dark at a low temperature (+4ºC). Shipment of samples with courier (2 days) at ambient temperature is acceptable. Before analysis, the samples should be diluted (if necessary) and transferred to autosampler vials and capped with a crimp-on cap. The autosampler should be refrigerated. Calibration samples should always be analyzed together with the unknown

samples in the same analytical series. For control of analytical performance in large sample series, quality control (QC) samples should be included within the analytical series. The QC samples should be spiked with appropriate concentrations of DNPZ within the calibration range. Method data (instrument parameters) should be stored routinely together with the sample data to verify the methodology used for analysis. Data (sample data and method parameters) should be collected and stored also on a back-up file.

The concentration of DNPZ in amine solvent should be measured in dilutions of amine solvent diluted to 1:100. Wash water is a dilute aqueous solution that may contain DNPZ and degradation products of DNPZ. DNPZ in wash water can be measured by direct injection of the wash water sample. As a main rule, flue gas absorption solutions may also be analyzed by direct injection, however, dilution may be necessary if the absorption solution contains acids, bases or other constituents in significant amounts.

CRITERIA FOR ACCEPTANCE

Acceptance criteria should be applied to chromatographic performance, mass spectrometric performance and the results of the QC samples. Chromatographic criteria: Peak shape should be symmetric and similar to a calibration standard with comparable concentration, the retention time should be within +/- 2% of the retention time of calibration standard. Mass spectrometric analysis: DNPZ has two transitions, and consequently, the ion ratio criteria (within +/- 20%) between two signals can be compared.

DATA TO BE RECORDED / METHOD OF ANALYSIS / DATA PRESENTATION

Raw data must be recorded as separate data files. A logic file name structure should be applied to the samples which make it easy and safe to identify analytical series (all the samples analyzed within the same series, together with calibrators and QC samples) as well as the individual unknown samples. Method parameters should be recorded together with raw data, this is normally handled automatically by the instrument software. This is obligatory to secure methodological traceability. It is recommended to calculate concentrations of analyte in unknown samples and QC samples as a batch process. This will allow for more efficient data handling.

UNCERTAINTY OF PROCEDURE

The relative uncertainties of the different steps of the methodological procedure should be estimated and tabulated as an uncertainty budget. The overall instrumental precision measured as % RSD (Relative Standard Deviation) is better than 3% (n=5) within the measuring range given above.

METHOD DESCRIPTION MONOETHANOLAMINE (MEA) BY LC-MS-MS-QQQ

APPROPRIATE IDENTIFICATION
MEA can be detected and identified by liquid chromatography combined with mass spectrometry (LC-MS-MS-QQQ).

SCOPE
Amine solvents, wash water and flue gas samples.

DESCRIPTION OF SAMPLES
MEA is an amine solvent (normally used as a single constituent in water). Wash water is a dilute aqueous solution that may contain MEA and degradation products of MEA. Flue gas samples may be dilute aqueous absorption solutions of varying composition, including acids, bases or other constituents in significant amounts.

CONCENTRATION RANGES TO BE DETERMINED
The calibration range may cover a range from 0.050 to 50 mg/L. If the concentration of MEA in the sample is higher, the sample should be diluted to a final concentration within the range given above.

INSTRUMENTATION / EQUIPMENT
An Agilent 1290/6460 liquid chromatography – triple quadrupole mass spectrometer (LC-MS-MS-QQQ) system may be used.

Chromatographic conditions:
Column: Ascentis Express RP-Amide (15 cm x 4.6 mm, 2.7 µm particle size)
Mobile phase: 25 mM formic acid
Flow 0.6 mL/min
Injection volume: 1 µL
Retention time MEA: ca. 2.0 min

Mass spectrometric conditions:
Ionization: Agilent Jet Stream (AJS) Electrospray ionization (ESI), Positive ion mode
Transition: m/z $(M+H)^+$ 62.1 → 44.2.

REFERENCE STANDARDS AND REFERENCE MATERIALS
MEA (monoethanolamine, ethanolamine, NH_2-CH_2-CH_2-OH, CAS No. 141-41-5, Mw 61.05 g/mol) (>99.5%), d4-MEA (deuterated MEA) (>98% D atom).

ENVIRONMENTAL CONDITIONS / STABILIZATION
Ambient conditions for operation, temperature: 15 to 35ºC, humidity 20 to 80% RH.

PROCEDURES
Samples should be contained in plastic (HDPE) containers. The containers should be stored dark at a low temperature (+4ºC). Shipment of samples with courier (2 days) at ambient temperature is acceptable. Before analysis, the samples should be diluted (if necessary) and transferred to autosampler vials and capped with a crimp-on cap. The autosampler should be refrigerated. Calibration samples should always be analyzed together with the unknown

samples in the same analytical series. For control of analytical performance in large sample series, quality control (QC) samples should be included within the analytical series. The QC samples should be spiked with appropriate concentrations of MEA within the calibration range. Method data (instrument parameters) should be stored routinely together with the sample data to verify the methodology used for analysis. Data (sample data and method parameters) should be collected and stored also on a back-up file.

The concentration of MEA in amine solvent should be measured in dilutions of amine solvent diluted 1:10 000. Wash water is a dilute aqueous solution that may contain MEA and degradation products of MEA, and dilution before analysis is generally necessary. The degree of dilution depends strongly on the specific sample. As a main rule, MEA in flue gas absorption solutions can be measured by direct injection of the flue gas sample, however, dilution may be necessary if the samples contain acids, bases or other constituents in significant amounts.

CRITERIA FOR ACCEPTANCE

Acceptance criteria should be applied to chromatographic performance, mass spectrometric performance and the results of the QC samples. Chromatographic criteria: Peak shape should be symmetric and similar to a calibration standard with comparable concentration, the retention time should be within +/- 2% of the retention time of calibration standard. Mass spectrometric analysis: Due to its low molecular weight, MEA has only one transition, and consequently, no ion ratio criteria (within +/- 20%) between two signals can be compared.

DATA TO BE RECORDED / METHOD OF ANALYSIS / DATA PRESENTATION

Raw data must be recorded as separate data files. A logic file name structure should be applied to the samples which make it easy and safe to identify analytical series (all the samples analyzed within the same series, together with calibrators and QC samples) as well as the individual unknown samples. Method parameters should be recorded together with raw data, this is normally handled automatically by the instrument software. This is obligatory to secure methodological traceability. It is recommended to calculate concentrations of analyte in unknown samples and QC samples as a batch process. This will allow for more efficient data handling.

UNCERTAINTY OF PROCEDURE

The relative uncertainties of the different steps of the methodological procedure should be estimated and tabulated as an uncertainty budget. The overall instrumental precision measured as % RSD (Relative Standard Deviation) is better than 3% (n=10) within the measuring range given above.

METHOD DESCRIPTION DIETHANOLAMINE (DEA) BY LC-MS-MS-QQQ

APPROPRIATE IDENTIFICATION
DEA can be detected and identified by liquid chromatography combined with mass spectrometry (LC-MS).

SCOPE
Amine solvents, wash water and flue gas samples.

DESCRIPTION OF SAMPLES
DEA is an amine solvent (normally used as a single constituent in water). DEA can also be measured as a minor compound in MEA. Wash water is a dilute aqueous solution that may contain DEA. Flue gas samples may be dilute aqueous absorption solutions of varying composition, including acids, bases or other constituents in significant amounts.

CONCENTRATION RANGES TO BE DETERMINED
The calibration range may cover a range from 1 µg/L to 10 mg/L. If the concentration of DEA in the sample is higher, the sample should be diluted to a final concentration within the range given above.

INSTRUMENTATION / EQUIPMENT
An Agilent 1290/6460 liquid chromatography – triple quadrupole mass spectrometer (LC-MS-MS-QQQ) system may be used.

Chromatographic conditions:
Column: Discovery HS-F5, (15cm x 2.1 mm, 3 µm)
Mobile phase: 12mM AmAc/MeOH – 10/90
Flow: 0.5 mL/min
Injection volume: 5 µL
Retention time DEA: 5.09 min

Mass spectrometric conditions:
Ionization: Agilent Jet Stream (AJS) Electrospray ionization (ESI), Positive ion mode
Transition: m/z $(M+H)^+$ 106.1 → 88.1 and 106.1 → 70.2

REFERENCE STANDARDS AND REFERENCE MATERIALS
DEA (diethanolamine, 2,2'-iminodiethanol, OH-CH_2-CH_2-NH-CH_2-CH_2-OH, CAS No. 111-42-2, Mw 105.14 g/mol) (>99.5%)
d8-DEA (deuterated DEA) CAS No. 103691-51-6 (>98% D atom).

ENVIRONMENTAL CONDITIONS / STABILIZATION
Ambient conditions for operation, temperature: 15 to 35ºC, humidity 20 to 80% RH.

PROCEDURES
Samples should be contained in plastic (HDPE) containers. The containers should be stored dark at a low temperature (+4ºC). Shipment of samples with courier (2 days) at ambient temperature is acceptable. Before analysis, the samples should be diluted (if necessary) and transferred to autosampler vials and capped with a crimp-on cap. The autosampler should be

refrigerated. Calibration samples should always be analyzed together with the unknown samples in the same analytical series. For control of analytical performance in large sample series, quality control (QC) samples should be included within the analytical series. The QC samples should be spiked with appropriate concentrations of DEA within the calibration range. Method data (instrument parameters) should be stored routinely together with the sample data to verify the methodology used for analysis. Data (sample data and method parameters) should be collected and stored also on a back-up file.

The concentration of DEA in amine solvent should be measured in dilutions of amine solvent diluted 1:10 000. Wash water is a dilute aqueous solution that may contain DEA and degradation products of DEA, and dilution before analysis is generally necessary. The degree of dilution depends strongly on the specific sample. As a main rule, DEA in flue gas absorption solutions can be measured by direct injection of the flue gas sample, however, dilution may be necessary if the samples contain acids, bases or other constituents in significant amounts.

CRITERIA FOR ACCEPTANCE

Acceptance criteria should be applied to chromatographic performance, mass spectrometric performance and the results of the QC samples. Chromatographic criteria: Peak shape should be symmetric and similar to a calibration standard with comparable concentration, the retention time should be within +/- 2% of the retention time of calibration standard. Mass spectrometric analysis: Due to its low molecular weight, DEA has only one transition, and consequently, no ion ratio criteria (within +/- 20%) between two signals can be compared.

DATA TO BE RECORDED / METHOD OF ANALYSIS / DATA PRESENTATION

Raw data must be recorded as separate data files. A logic file name structure should be applied to the samples which make it easy and safe to identify analytical series (all the samples analyzed within the same series, together with calibrators and QC samples) as well as the individual unknown samples. Method parameters should be recorded together with raw data, this is normally handled automatically by the instrument software. This is obligatory to secure methodological traceability. It is recommended to calculate concentrations of analyte in unknown samples and QC samples as a batch process. This will allow for more efficient data handling.

UNCERTAINTY OF PROCEDURE

The relative uncertainties of the different steps of the methodological procedure should be estimated and tabulated as an uncertainty budget. The overall instrumental precision measured as % RSD (Relative Standard Deviation) is better than 3% (n=5) within the measuring range given above.

METHOD DESCRIPTION PIPERAZINE (PZ) BY LC-MS-MS-QQQ

APPROPRIATE IDENTIFICATION
PZ can be detected and identified by liquid chromatography combined with mass spectrometry (LC-MS).

SCOPE
Amine solvents, wash water and flue gas samples.

DESCRIPTION OF SAMPLES
PZ is an amine solvent (used as a single constituent in water or together with AMP). Wash water is a dilute aqueous solution that be may contain PZ. Flue gas samples may be dilute aqueous absorption solutions of varying composition, including acids, bases or other constituents in significant amounts.

CONCENTRATION RANGES TO BE DETERMINED
The calibration range may cover a range from 0.086 to 86 mg/L. If the concentration of PZ in the sample is higher, the sample should be diluted to a final concentration within the range given above.

INSTRUMENTATION / EQUIPMENT
An Agilent 1290/6460 liquid chromatography – triple quadrupole mass spectrometer (LC-MS-MS-QQQ) system may be used.

Chromatographic conditions:
Column: Ascentis Express RP-Amide (15 cm x 4.6 mm, 2.7 µm particle size)
Mobile phase: 25 mM formic acid
Flow 0.5 mL/min
Injection volume: 0.5 µL
Retention time PZ: ca. 2.2 min

Mass spectrometric conditions:
Ionization: Agilent Jet Stream (AJS) Electrospray ionization (ESI), Positive ion mode
Transition: m/z $(M+H)^+$ 87.1 → 44.2.

REFERENCE STANDARDS AND REFERENCE MATERIALS
PZ (piperazine, diethylenediamine, $C_4H_{10}N_2$, CAS No. 110-85-0, Mw 86.14 g/mol) (>99.5%), d8-PZ (deuterated PZ), CAS No. 134628-42-5, Mw 94.19 g/mol (>98.7% D atom)

ENVIRONMENTAL CONDITIONS / STABILIZATION
Ambient conditions for operation, temperature: 15 to 35ºC, humidity 20 to 80% RH.

PROCEDURES
Samples should be contained in plastic (HDPE) containers. The containers should be stored dark at a low temperature (+4ºC). Shipment of samples with courier (2 days) at ambient temperature is acceptable. Before analysis, the samples should be diluted (if necessary) and transferred to autosampler vials and capped with a crimp-on cap. The autosampler should be refrigerated. Calibration samples should always be analyzed together with the unknown

samples in the same analytical series. For control of analytical performance in large sample series, quality control (QC) samples should be included within the analytical series. The QC samples should be spiked with appropriate concentrations of PZ within the calibration range. Method data (instrument parameters) should be stored routinely together with the sample data to verify the methodology used for analysis. Data (sample data and method parameters) should be collected and stored also on a back-up file.

The concentration of PZ in amine solvent should be measured in dilutions of amine solvent diluted 1:10 000. Wash water is a dilute aqueous solution that may contain PZ and degradation products of PZ, and dilution before analysis is generally necessary. The degree of dilution depends strongly on the specific sample. As a main rule, PZ in flue gas absorption solutions can be measured by direct injection of the flue gas sample, however, dilution may be necessary if the samples contain acids, bases or other constituents in significant amounts.

CRITERIA FOR ACCEPTANCE

Acceptance criteria should be applied to chromatographic performance, mass spectrometric performance and the results of the QC samples. Chromatographic criteria: Peak shape should be symmetric and similar to a calibration standard with comparable concentration, the retention time should be within +/- 2% of the retention time of calibration standard. Mass spectrometric analysis: Due to its low molecular weight, PZ has only one transition, and consequently, no ion ratio criteria (within +/- 20%) between two signals can be compared.

DATA TO BE RECORDED / METHOD OF ANALYSIS / DATA PRESENTATION

Raw data must be recorded as separate data files. A logic file name structure should be applied to the samples which make it easy and safe to identify analytical series (all the samples analyzed within the same series, together with calibrators and QC samples) as well as the individual unknown samples. Method parameters should be recorded together with raw data, this is normally handled automatically by the instrument software. This is obligatory to secure methodological traceability. It is recommended to calculate concentrations of analyte in unknown samples and QC samples as a batch process. This will allow for more efficient data handling.

UNCERTAINTY OF PROCEDURE

The relative uncertainties of the different steps of the methodological procedure should be estimated and tabulated as an uncertainty budget. The overall instrumental precision measured as % RSD (Relative Standard Deviation) is better than 3% (n=10) within the measuring range given above.

METHOD DESCRIPTION 2-AMINO-2-METHYL-1-PROPANOL (AMP) BY LC-MS-MS-QQQ

APPROPRIATE IDENTIFICATION
AMP can be detected and identified by liquid chromatography combined with mass spectrometry (LC-MS).

SCOPE
Amine solvents, wash water and flue gas samples.

DESCRIPTION OF SAMPLES
AMP is an amine solvent (normally used as a single constituent in water and together with PZ). Wash water is a dilute aqueous solution that may contain AMP and degradation products of AMPFlue gas samples may be dilute aqueous absorption solutions of varying composition, including acids, bases or other constituents in significant amounts.

CONCENTRATION RANGES TO BE DETERMINED
The calibration range may cover a range from 0.089 to 89 mg/L. If the concentration of AMP in the sample is higher, the sample should be diluted to a final concentration within the range given above.

INSTRUMENTATION / EQUIPMENT
An Agilent 1290/6460 liquid chromatography – triple quadrupole mass spectrometer (LC-MS-MS-QQQ) system may be used.

Chromatographic conditions:
Column: Ascentis Express RP-Amide (15 cm x 4.6 mm, 2.7 µm particle size)
Mobile phase: 25 mM formic acid
Flow 0.5 mL/min
Injection volume: 0.5 µL
Retention time AMP: ca. 2.56 min

Mass spectrometric conditions:
Ionization: Agilent Jet Stream (AJS) Electrospray ionization (ESI), Positive ion mode
Transition: m/z $(M+H)^+$ 90.1 → 55.2

REFERENCE STANDARDS AND REFERENCE MATERIALS
AMP (2-amino-2-methyl-1-propanol, 2-aminoisobutanol, NH_2-C$(CH_2)_2$-CH_2-OH, CAS No. 124-68-5, Mw 89.14 g/mol) (>99.5%)

ENVIRONMENTAL CONDITIONS / STABILIZATION
Ambient conditions for operation, temperature: 15 to 35ºC, humidity 20 to 80% RH.

PROCEDURES
Samples should be contained in plastic (HDPE) containers. The containers should be stored dark at a low temperature (+4ºC). Shipment of samples with courier (2 days) at ambient temperature is acceptable. Before analysis, the samples should be diluted (if necessary) and transferred to autosampler vials and capped with a crimp-on cap. The autosampler should be refrigerated. Calibration samples should always be analyzed together with the unknown

samples in the same analytical series. For control of analytical performance in large sample series, quality control (QC) samples should be included within the analytical series. The QC samples should be spiked with appropriate concentrations of AMP within the calibration range. Method data (instrument parameters) should be stored routinely together with the sample data to verify the methodology used for analysis. Data (sample data and method parameters) should be collected and stored also on a back-up file.

The concentration of AMP in amine solvent should be measured in dilutions of amine solvent diluted 1:10 000. Wash water is a dilute aqueous solution that may contain AMP and degradation products of AMP, and dilution before analysis is generally necessary. The degree of dilution depends strongly on the specific sample. As a main rule, AMP in flue gas absorption solutions can be measured by direct injection of the flue gas sample, however, dilution may be necessary if the samples contain acids, bases or other constituents in significant amounts.

CRITERIA FOR ACCEPTANCE

Acceptance criteria should be applied to chromatographic performance, mass spectrometric performance and the results of the QC samples. Chromatographic criteria: Peak shape should be symmetric and similar to a calibration standard with comparable concentration, the retention time should be within +/- 2% of the retention time of calibration standard. Mass spectrometric analysis: Due to its low molecular weight, AMP has only one transition, and consequently, no ion ratio criteria (within +/- 20%) between two signals can be compared.

DATA TO BE RECORDED / METHOD OF ANALYSIS / DATA PRESENTATION

Raw data must be recorded as separate data files. A logic file name structure should be applied to the samples which make it easy and safe to identify analytical series (all the samples analyzed within the same series, together with calibrators and QC samples) as well as the individual unknown samples. Method parameters should be recorded together with raw data, this is normally handled automatically by the instrument software. This is obligatory to secure methodological traceability. It is recommended to calculate concentrations of analyte in unknown samples and QC samples as a batch process. This will allow for more efficient data handling.

UNCERTAINTY OF PROCEDURE

The relative uncertainties of the different steps of the methodological procedure should be estimated and tabulated as an uncertainty budget. The overall instrumental precision measured as % RSD (Relative Standard Deviation) is better than 3% (n=10) within the measuring range given above.

METHOD DESCRIPTION N-METHYLDIETHANOLAMINE (MDEA) BY LC-MS-MS-QQQ

APPROPRIATE IDENTIFICATION
MDEA can be detected and identified by liquid chromatography combined with mass spectrometry (LC-MS).

SCOPE
Amine solvents, wash water and flue gas samples.

DESCRIPTION OF SAMPLES
MDEA is an amine solvent (normally used as a single constituent in water). Wash water is a dilute aqueous solution that may contain MDEA and degradation products of MDEA. Flue gas samples may be dilute aqueous absorption solutions of varying composition, including acids, bases or other constituents in significant amounts.

CONCENTRATION RANGES TO BE DETERMINED
The calibration range may cover a range from 1 µg/L to 120 mg/L. If the concentration of MDEA in the sample is higher, the sample should be diluted to a final concentration within the range given above.

INSTRUMENTATION / EQUIPMENT
An Agilent 1290/6460 liquid chromatography – triple quadrupole mass spectrometer (LC-MS-MS-QQQ) system may be used.

Chromatographic conditions:
Column: Ascentis Express RP-Amide (15 cm x 4.6 mm, 2.7 µm particle size)
Mobile phase: 25 mM formic acid/MeOH – 70/30
Flow: 0.5 mL/min
Injection volume: 2 µL
Retention time MDEA: ca. 2.37 min

Mass spectrometric conditions:
Ionization: Agilent Jet Stream (AJS) Electrospray ionization (ESI), Positive ion mode
Transition: m/z $(M+H)^+$ 120.1 → 58.1 and 120.1 → 102,1

REFERENCE STANDARDS AND REFERENCE MATERIALS
MDEA (Bis(2-hydroxyethyl)methylamine, N-methyldiethanolamine, OH- CH_2-CH_2-N(CH_3)-CH_2-CH_2-OH, CAS No. 105-59-9, Mw 119.16 g/mol) (>99.5%)

ENVIRONMENTAL CONDITIONS / STABILIZATION
Ambient conditions for operation, temperature: 15 to 35ºC, humidity 20 to 80% RH.

PROCEDURES
Samples should be contained in plastic (HDPE) containers. The containers should be stored dark at a low temperature (+4ºC). Shipment of samples with courier (2 days) at ambient temperature is acceptable. Before analysis, the samples should be diluted (if necessary) and transferred to autosampler vials and capped with a crimp-on cap. The autosampler should be refrigerated. Calibration samples should always be analyzed together with the unknown

samples in the same analytical series. For control of analytical performance in large sample series, quality control (QC) samples should be included within the analytical series. The QC samples should be spiked with appropriate concentrations of MDEA within the calibration range. Method data (instrument parameters) should be stored routinely together with the sample data to verify the methodology used for analysis. Data (sample data and method parameters) should be collected and stored also on a back-up file.

The concentration of MDEA in amine solvent should be measured in dilutions of amine solvent diluted 1:10 000. Wash water is a dilute aqueous solution that may contain MDEA and degradation products of MDEA, and dilution before analysis is generally necessary. The degree of dilution depends strongly on the specific sample. As a main rule, MDEA in flue gas absorption solutions can be measured by direct injection of the flue gas sample, however, dilution may be necessary if the samples contain acids, bases or other constituents in significant amounts.

CRITERIA FOR ACCEPTANCE

Acceptance criteria should be applied to chromatographic performance, mass spectrometric performance and the results of the QC samples. Chromatographic criteria: Peak shape should be symmetric and similar to a calibration standard with comparable concentration, the retention time should be within +/- 2% of the retention time of calibration standard. Mass spectrometric analysis: MDEA has two transitions, and consequently, the ion ratio criteria (within +/- 20%) between two signals can be compared.

DATA TO BE RECORDED / METHOD OF ANALYSIS / DATA PRESENTATION

Raw data must be recorded as separate data files. A logic file name structure should be applied to the samples which make it easy and safe to identify analytical series (all the samples analyzed within the same series, together with calibrators and QC samples) as well as the individual unknown samples. Method parameters should be recorded together with raw data, this is normally handled automatically by the instrument software. This is obligatory to secure methodological traceability. It is recommended to calculate concentrations of analyte in unknown samples and QC samples as a batch process. This will allow for more efficient data handling.

UNCERTAINTY OF PROCEDURE

The relative uncertainties of the different steps of the methodological procedure should be estimated and tabulated as an uncertainty budget. The overall instrumental precision measured as % RSD (Relative Standard Deviation) is better than 3% (n=5) within the measuring range given above.

METHOD DESCRIPTION 1.2-DIAMINOETHANE (EDA) BY LC-MS-MS-QQQ

APPROPRIATE IDENTIFICATION
EDA can be detected and identified by liquid chromatography combined with triple mass spectrometry (LC-MS-MS-QQQ).

SCOPE
Amine solvents, wash water and flue gas samples.

DESCRIPTION OF SAMPLES
EDA is an amine solvent (normally used as a single constituent in water). Wash water is a dilute aqueous solution that may contain EDA and degradation products of EDA. Flue gas samples may be dilute aqueous absorption solutions of varying composition, including acids, bases or other constituents in significant amounts.

CONCENTRATION RANGES TO BE DETERMINED
The calibration range may cover a range from a level yet to be determined to 50 mg/L. If the concentration of EDA in the sample is higher, the sample should be diluted to a final concentration within the range given above.

INSTRUMENTATION / EQUIPMENT
An Agilent 1290/6460 liquid chromatography – triple quadrupole mass spectrometer (LC-MS-MS-QQQ) system may be used.

Chromatographic conditions:
Column: Ascentis Express RP-Amide (15 cm x 4.6 mm, 2.7 µm particle size)
Mobile phase: 25 mM formic acid, flow 0.5 mL/min
Injection volume: yet to be determined
Retention time EDA: ca. 2.22 min

Mass spectrometric conditions:
Ionization: Agilent Jet Stream (AJS) Electrospray ionization (ESI), Positive ion mode
Transition: m/z $(M+H)^+$ 61.1 → 44.1.

REFERENCE STANDARDS AND REFERENCE MATERIALS
EDA (1.2-diaminoethane, edamine, NH_2-CH_2-CH_2-NH_2, CAS No. 107-15-3, Mw 60.1 g/mol)

ENVIRONMENTAL CONDITIONS / STABILIZATION
Ambient conditions for operation, temperature: 15 to 35ºC, humidity 20 to 80% RH.

PROCEDURES
Samples should be contained in plastic (HDPE) containers. The containers should be stored dark at a low temperature (+4ºC). Shipment of samples with courier (2 days) at ambient temperature is acceptable. Before analysis, the samples should be diluted (if necessary) and transferred to autosampler vials and capped with a crimp-on cap. The autosampler should be refrigerated. Calibration samples should always be analyzed together with the unknown samples in the same analytical series. For control of analytical performance in large sample series, quality control (QC) samples should be included within the analytical series. The QC

samples should be spiked with appropriate concentrations of EDA within the calibration range. Method data (instrument parameters) should be stored routinely together with the sample data to verify the methodology used for analysis. Data (sample data and method parameters) should be collected and stored also on a back-up file.

The concentration of EDA in amine solvent should be measured in dilutions of amine solvent diluted 1:10 000. Wash water is a dilute aqueous solution that may contain EDA and degradation products of EDA, and dilution before analysis is generally necessary. The degree of dilution depends strongly on the specific sample. As a main rule, EDA in flue gas absorption solutions can be measured by direct injection of the flue gas sample, however, dilution may be necessary if the samples contain acids, bases or other constituents in significant amounts.

CRITERIA FOR ACCEPTANCE

Acceptance criteria should be applied to chromatographic performance, mass spectrometric performance and the results of the QC samples. Chromatographic criteria: Peak shape should be symmetric and similar to a calibration standard with comparable concentration; the retention time should be within +/- 2% of the retention time of calibration standard. Mass spectrometric analysis: Due to its low molecular weight, EDA has only one transition, and consequently, no ion ratio criteria (within +/- 20%) between two signals can be compared.

DATA TO BE RECORDED / METHOD OF ANALYSIS / DATA PRESENTATION

Raw data must be recorded as separate data files. A logic file name structure should be applied to the samples which make it easy and safe to identify analytical series (all the samples analyzed within the same series, together with calibrators and QC samples) as well as the individual unknown samples. Method parameters should be recorded together with raw data, this is normally handled automatically by the instrument software. This is obligatory to secure methodological traceability. It is recommended to calculate concentrations of analyte in unknown samples and QC samples as a batch process. This will allow for more efficient data handling.

UNCERTAINTY OF PROCEDURE

Yet to be determined.

METHOD DESCRIPTION FORMAMIDE BY LC-MS-MS-QQQ

APPROPRIATE IDENTIFICATION
Formamide can be detected and identified by liquid chromatography combined with mass spectrometry (LC-MS).

SCOPE
Wash water and flue gas samples.

DESCRIPTION OF SAMPLES
Formamide is a degradation product that may occur in amine solvents. Wash water is a dilute aqueous solution that may contain formamide and degradation products of formamide. Flue gas samples may be dilute aqueous absorption solutions of varying composition, including acids, bases or other constituents in significant amounts.

CONCENTRATION RANGES TO BE DETERMINED
The calibration range may cover a range from 10 to 10 000 µg/L. If the concentration of formamide in the sample is higher, the sample should be diluted to a final concentration within the range given above.

INSTRUMENTATION / EQUIPMENT
An Agilent 1290/6460 liquid chromatography – triple quadrupole mass spectrometer (LC-MS-MS-QQQ) system may be used.

Chromatographic conditions:
Column: Discovery HS F5 (15 cm x 4.6 mm, 3 µm particle size)
Mobile phase: 25 mM formic acid/MeOH - (90/10)
Flow: 1 mL/min
Injection volume: 5 µL
Retention time formamide: ca. 2.49 min

Mass spectrometric conditions:
Ionization: Agilent Jet Stream (AJS) Electrospray ionization (ESI), Positive ion mode
Transition: m/z $(M+H)^+$ 46,1 → 46,1 (SIM)

REFERENCE STANDARDS AND REFERENCE MATERIALS
Formamide (methanamide, formamide, NH_2-COH, CAS No. 75-12-7, Mw 45.04 g/mol)

ENVIRONMENTAL CONDITIONS / STABILIZATION
Ambient conditions for operation, temperature: 15 to 35ºC, humidity 20 to 80% RH.

PROCEDURES
Samples should be contained in plastic (HDPE) containers. The containers should be stored dark at a low temperature (+4ºC). Shipment of samples with courier (2 days) at ambient temperature is acceptable. Before analysis, the samples should be diluted (if necessary) and transferred to autosampler vials and capped with a crimp-on cap. The autosampler should be refrigerated. Calibration samples should always be analyzed together with the unknown samples in the same analytical series. For control of analytical performance in large sample

series, quality control (QC) samples should be included within the analytical series. The QC samples should be spiked with appropriate concentrations of formamide within the calibration range. Method data (instrument parameters) should be stored routinely together with the sample data to verify the methodology used for analysis. Data (sample data and method parameters) should be collected and stored also on a back-up file.

Wash water is a dilute aqueous solution that may contain formamide and degradation products of formamide. Formamide can be measured by direct injection of this wash water sample. As a main rule, flue gas absorption solutions may also be analyzed by direct injection, however, dilution may be necessary if the absorption solution contains acids, bases or other constituents in significant amounts.

CRITERIA FOR ACCEPTANCE

Acceptance criteria should be applied to chromatographic performance, mass spectrometric performance and the results of the QC samples. Chromatographic criteria: Peak shape should be symmetric and similar to a calibration standard with comparable concentration, the retention time should be within +/- 2% of the retention time of calibration standard. Mass spectrometric analysis: Due to its low molecular weight, formamide has no transitions, and consequently, no ion ratio criteria (within +/- 20%) between two signals can be compared. Formamide is analyzed in SIM mode.

DATA TO BE RECORDED / METHOD OF ANALYSIS / DATA PRESENTATION

Raw data must be recorded as separate data files. A logic file name structure should be applied to the samples which make it easy and safe to identify analytical series (all the samples analyzed within the same series, together with calibrators and QC samples) as well as the individual unknown samples. Method parameters should be recorded together with raw data, this is normally handled automatically by the instrument software. This is obligatory to secure methodological traceability. It is recommended to calculate concentrations of analyte in unknown samples and QC samples as a batch process. This will allow for more efficient data handling.

UNCERTAINTY OF PROCEDURE

The relative uncertainties of the different steps of the methodological procedure should be estimated and tabulated as an uncertainty budget. The overall instrumental precision measured as % RSD (Relative Standard Deviation) is better than 3% (n=5) within the measuring range given above.

METHOD DESCRIPTION ACETAMIDE BY LC-MS-MS-QQQ

APPROPRIATE IDENTIFICATION
Acetamide can be detected and identified by liquid chromatography combined with mass spectrometry (LC-MS).

SCOPE
Wash water and flue gas samples.

DESCRIPTION OF SAMPLES
Acetamide is a degradation product that may occur in amine solvents. Wash water is a dilute aqueous solution that may contain acetamide. Flue gas samples may be dilute aqueous absorption solutions of varying composition, including acids, bases or other constituents in significant amounts.

CONCENTRATION RANGES TO BE DETERMINED
The calibration range may cover a range from 10 to 10 000 µg/L. If the concentration of acetamide in the sample is higher, the sample should be diluted to a final concentration within the range given above.

INSTRUMENTATION / EQUIPMENT
An Agilent 1290/6460 liquid chromatography – triple quadrupole mass spectrometer (LC-MS-MS-QQQ) system may be used.

Chromatographic conditions:
Column: Discovery HS F5 (15 cm x 4.6 mm, 3 µm particle size)
Mobile phase: 25 mM formic acid/MeOH - (90/10)
Flow: 1 mL/min
Injection volume: 5 µL
Retention time formamide: ca. 3.34 min

Mass spectrometric conditions:
Ionization: Agilent Jet Stream (AJS) Electrospray ionization (ESI), Positive ion mode
Transition: m/z $(M+H)^+$ 60.0 → 43.0

REFERENCE STANDARDS AND REFERENCE MATERIALS
Acetamide (ethanamide, acetamide, NH_2-CO-CH_3, CAS No. 60-35-5, Mw 59.07 g/mol) (>99.5%),
d5-acetamide (deuterated acetamide) CAS No. 33675-83-1, Mw 64.10 g/mol (>98% D atom).

ENVIRONMENTAL CONDITIONS / STABILIZATION
Ambient conditions for operation, temperature: 15 to 35ºC, humidity 20 to 80% RH.

PROCEDURES
Samples should be contained in plastic (HDPE) containers. The containers should be stored dark at a low temperature (+4ºC). Shipment of samples with courier (2 days) at ambient temperature is acceptable. Before analysis, the samples should be diluted (if necessary) and transferred to autosampler vials and capped with a crimp-on cap. The autosampler should be

refrigerated. Calibration samples should always be analyzed together with the unknown samples in the same analytical series. For control of analytical performance in large sample series, quality control (QC) samples should be included within the analytical series. The QC samples should be spiked with appropriate concentrations of acetamide within the calibration range. Method data (instrument parameters) should be stored routinely together with the sample data to verify the methodology used for analysis. Data (sample data and method parameters) should be collected and stored also on a back-up file.

Wash water is a dilute aqueous solution that may contain acetamide. Acetamide can be measured by direct injection of the wash water sample. As a main rule, flue gas absorption solutions may also be analyzed by direct injection, however, dilution may be necessary if the absorption solution contains acids, bases or other constituents in significant amounts.

CRITERIA FOR ACCEPTANCE

Acceptance criteria should be applied to chromatographic performance, mass spectrometric performance and the results of the QC samples. Chromatographic criteria: Peak shape should be symmetric and similar to a calibration standard with comparable concentration, the retention time should be within +/- 2% of the retention time of calibration standard. Mass spectrometric analysis: Due to its low molecular weight, acetamide has only one transition, and consequently, no ion ratio criteria (within +/- 20%) between two signals can be compared.

DATA TO BE RECORDED / METHOD OF ANALYSIS / DATA PRESENTATION

Raw data must be recorded as separate data files. A logic file name structure should be applied to the samples which make it easy and safe to identify analytical series (all the samples analyzed within the same series, together with calibrators and QC samples) as well as the individual unknown samples. Method parameters should be recorded together with raw data, this is normally handled automatically by the instrument software. This is obligatory to secure methodological traceability. It is recommended to calculate concentrations of analyte in unknown samples and QC samples as a batch process. This will allow for more efficient data handling.

UNCERTAINTY OF PROCEDURE

The relative uncertainties of the different steps of the methodological procedure should be estimated and tabulated as an uncertainty budget. The overall instrumental precision measured as % RSD (Relative Standard Deviation) is better than 3% (n=5) within the measuring range given above.

METHOD DESCRIPTION FORMALDEHYDE BY LC-MS-MS-QQQ

APPROPRIATE IDENTIFICATION
Formaldehyde-DNPH can be detected and identified by liquid chromatography combined with mass spectrometry (LC-MS).

SCOPE
Wash water and flue gas samples.

DESCRIPTION OF SAMPLES
Formaldehyde is a degradation product that may occur in amine solvent. Wash water is a dilute aqueous solution that be may contain formaldehyde and degradation products of formaldehyde. Flue gas samples may be dilute aqueous absorption solutions of varying composition, including acids, bases or other constituents in significant amounts.

CONCENTRATION RANGES TO BE DETERMINED
The calibration range may cover a range from 10 to 10 000 µg/L. If the concentration of formaldehyde in the sample is higher, the sample should be diluted to a final concentration within the range given above.

INSTRUMENTATION / EQUIPMENT
An Agilent 1290/6460 liquid chromatography – triple quadrupole mass spectrometer (LC-MS-MS-QQQ) system may be used.

Chromatographic conditions:
Column: Ascentis Express C8 (7.5 cm x 2.1 mm, 2.7 µm particle size)
Mobile phase: 12 mM AmAc/Acetonitrile, 55/45
Flow: 0.2 mL/min
Injection volume: 1 µL
Retention time formaldehyde-DNPH: 3.1 min

Mass spectrometric conditions:
Ionization: Agilent Jet Stream (AJS) Negative ionization
Transition: m/z (M-1): 209.1 → 46.0 MS-MS
209.1 → 120.8 MS-MS

REFERENCE STANDARDS AND REFERENCE MATERIALS
Formaldehyde, CAS No. 50-00-0, Mw 30.03 g/mol (>99.5%),
2.4-Dinitrophenylhydrazine, CAS 119-26-6, Mw 198.14 (>= 99.0%)

ENVIRONMENTAL CONDITIONS / STABILIZATION
Ambient conditions for operation, temperature: 15 to 35ºC, humidity 20 to 80% RH.

PROCEDURES
Samples should be contained in plastic (HDPE) containers. The containers should be stored dark at a low temperature (+4ºC). Shipment of samples with courier (2 days) at ambient temperature is acceptable.

Sample preparation: 50 mg of DNPH is dissolved in 20 mL of acetonitrile and acidified with 0,4mL formic acid. The solution is stable for one week when stored at 4°C.
100 µL of the DNPH is transferred to a vial containing an insert, and 100 µL of sample/calibration standard is added. Mix 3-4 times in the tip of the pipette. Cap the vials and incubate in room temperature for 1 hour. Transfer the vials to the LC-MS tray. It's important that the samples are cooled (6-8°C) while analyzed. This to stop any further derivatization in the sample mix.

Formaldehyde-DNPH can be measured by direct injection of the wash water or flue gas sample, after derivatization with DNPH. As a main rule, the absorption solutions may be analyzed by direct injection, however, dilution may be necessary if the absorption solution contains acids, bases or other constituents in significant amounts.

Calibration samples should always be analyzed together with the unknown samples in the same analytical series. For control of analytical performance in large sample series, quality control (QC) samples should be included within the analytical series. The QC samples should be spiked with appropriate concentrations of formaldehyde within the calibration range. Method data (instrument parameters) should be stored routinely together with the sample data to verify the methodology used for analysis. Data (sample data and method parameters) should be collected and stored also on a back-up file.

CRITERIA FOR ACCEPTANCE
Acceptance criteria should be applied to chromatographic performance, mass spectrometric performance and the results of the QC samples. Chromatographic criteria: Peak shape should be symmetric and similar to a calibration standard with comparable concentration, the retention time should be within +/- 2% of the retention time of calibration standard. Mass spectrometric analysis: Formaldehyde has two transitions, and the ion ratio criteria (within +/- 20%) between two signals can be compared.

DATA TO BE RECORDED / METHOD OF ANALYSIS / DATA PRESENTATION
Raw data must be recorded as separate data files. A logic file name structure should be applied to the samples which make it easy and safe to identify analytical series (all the samples analyzed within the same series, together with calibrators and QC samples) as well as the individual unknown samples. Method parameters should be recorded together with raw data, this is normally handled automatically by the instrument software. This is obligatory to secure methodological traceability. It is recommended to calculate concentrations of analyte in unknown samples and QC samples as a batch process. This will allow for more efficient data handling.

UNCERTAINTY OF PROCEDURE
The relative uncertainties of the different steps of the methodological procedure should be estimated and tabulated as an uncertainty budget. The overall instrumental precision measured as % RSD (Relative Standard Deviation) is better than 3% (n=5) within the measuring range given above.

METHOD DESCRIPTION ACETALDEHYDE BY LC-MS-MS-QQQ

APPROPRIATE IDENTIFICATION
Acetaldehyde-DNPH can be detected and identified by liquid chromatography combined with mass spectrometry (LC-MS).

SCOPE
Wash water and flue gas samples.

DESCRIPTION OF SAMPLES
Acetaldehyde is a degradation product that may occur in amine solvents. Wash water is a dilute aqueous solution that be may contain acetaldehyde and degradation products of formaldehyde. Flue gas samples may be dilute aqueous absorption solutions of varying composition, including acids, bases or other constituents in significant amounts.

CONCENTRATION RANGES TO BE DETERMINED
The calibration range may cover a range from 10 to 10 000 µg/L. If the concentration of formaldehyde in the sample is higher, the sample should be diluted to a final concentration within the range given above.

INSTRUMENTATION / EQUIPMENT
An Agilent 1290/6460 liquid chromatography – triple quadrupole mass spectrometer (LC-MS-MS-QQQ) system may be used.

Chromatographic conditions:
Column: Ascentis Express C8 (7.5 cm x 2.1 mm, 2.7 µm particle size)
Mobile phase: 12 mM AmAc/Acetonitrile, 55/45
Flow: 0.2 mL/min
Injection volume: 1 µL
Retention time acetaldehyde-DNPH: 4.2 min

Mass spectrometric conditions:
Ionization: Agilent Jet Stream (AJS) Negative ionization
Transition: m/z (M-1): 223.1 → 46.0 MS-MS
223.1 → 163.0 MS-MS

REFERENCE STANDARDS AND REFERENCE MATERIALS
Acetaldehyde, CAS No. 75-07-0, Mw 44.05 g/mol (>99.5%),
2.4-Dinitrophenylhydrazine, CAS 119-26-6, Mw 198.14 (>= 99.0%)

ENVIRONMENTAL CONDITIONS / STABILIZATION
Ambient conditions for operation, temperature: 15 to 35ºC, humidity 20 to 80% RH.

PROCEDURES
Samples should be contained in plastic (HDPE) containers. The containers should be stored dark at a low temperature (+4ºC). Shipment of samples with courier (2 days) at ambient temperature is acceptable.

Sample preparation: 50 mg of DNPH is dissolved in 20 mL of acetonitrile and acidified with 0,4mL formic acid. The solution is stable for one week when stored at 4°C.
100 µL of the DNPH is transferred to a vial containing an insert, and 100 µL of sample/calibration standard is added. Mix 3-4 times in the tip of the pipette. Cap the vials and incubate in room temperature for 1 hour. Transfer the vials to the LC-MS tray. It's important that the samples are cooled (6-8°C) while analyzed. This to stop any further derivatization in the sample mix.

Acetaldehyde-DNPH can be measured by direct injection of the wash water or flue gas samples after derivatization with DNPH. As a main rule, the absorption solutions may be analyzed by direct injection, however, dilution may be necessary if the absorption solution contains acids, bases or other constituents in significant amounts.

Calibration samples should always be analyzed together with the unknown samples in the same analytical series. For control of analytical performance in large sample series, quality control (QC) samples should be included within the analytical series. The QC samples should be spiked with appropriate concentrations of formaldehyde within the calibration range. Method data (instrument parameters) should be stored routinely together with the sample data to verify the methodology used for analysis. Data (sample data and method parameters) should be collected and stored also on a back-up file.

CRITERIA FOR ACCEPTANCE
Acceptance criteria should be applied to chromatographic performance, mass spectrometric performance and the results of the QC samples. Chromatographic criteria: Peak shape should be symmetric and similar to a calibration standard with comparable concentration, the retention time should be within +/- 2% of the retention time of calibration standard. Mass spectrometric analysis: Acetaldehyde has two transitions, and the ion ratio criteria (within +/- 20%) between two signals can be compared.

DATA TO BE RECORDED / METHOD OF ANALYSIS / DATA PRESENTATION
Raw data must be recorded as separate data files. A logic file name structure should be applied to the samples which make it easy and safe to identify analytical series (all the samples analyzed within the same series, together with calibrators and QC samples) as well as the individual unknown samples. Method parameters should be recorded together with raw data, this is normally handled automatically by the instrument software. This is obligatory to secure methodological traceability. It is recommended to calculate concentrations of analyte in unknown samples and QC samples as a batch process. This will allow for more efficient data handling.

UNCERTAINTY OF PROCEDURE
The relative uncertainties of the different steps of the methodological procedure should be estimated and tabulated as an uncertainty budget. The overall instrumental precision measured as % RSD (Relative Standard Deviation) is better than 3% (n=5) within the measuring range given above.

METHOD DESCRIPTION ALKYL AMINES AND AMMONIA (NH_3) BY GC-MS

APPROPRIATE IDENTIFICATION

Alkyl amines and NH_3 can be detected and identified by gas chromatography combined with mass spectrometry (GC-MS).

SCOPE

Wash water and flue gas samples.

DESCRIPTION OF SAMPLES

Wash water (dilute aqueous solution) and flue gas (dilute aqueous absorption solutions of varying composition) may contain alkyl amines and NH_3. The detection of alkyl amines and NH_3 is based on measuring the corresponding BSC derivatives.

CONCENTRATION RANGES TO BE DETERMINED

The calibration range for alkyl amines cover a range from 1 to 1 000 µg/L, and for NH_3 a range from 1 to 1 000 mg/L.

INSTRUMENTATION / EQUIPMENT

An Agilent 7890 A gas chromatography – mass spectrometer (GC-MS) system is used.

Chromatographic conditions:

Column:	WCOT Fused Silica CP-volamine (CP-7447): 30m x 320 µm
Oven	50C˚ for 2 min, then 20C˚/min to 250C˚ for 12 min
Injection volum	1 µl
Injection temperature	250C˚
Injection mode	Split (50:1)
Transfer line heather	250C˚
Acquisition mode	SIM
MS source temperature	230C˚
MS quad temperature	150C˚

Retention time (RT), ions and dwell:

Derivatives products of	**RT**	**Ion**	**Dwell**
Methylamine	15,80	171	100
Dimethylamine	15,65	185	100
Ethylamine	16,51	170	100
Diethylamine	17,81	198	100
NH_3	15,55	157	100
Internal standard, methylbutylamine	20,49	185	100

REFERENCE STANDARDS AND REFERENCE MATERIALS

Dimethylamine, 40 % solution in water (C_2H_7N, CAS No. 124-40-3, Mw 45.08 g/mol) (AC-163670010), Methylamine, 40 % solution in water (CH_5N, CAS No. 74-89-5, Mw 31.06 g/mol) (AC-1262300100), Ethylamine, 70 % solution in water (C_2H_7N, CAS No. 75-04-7,

Mw 45.08 g/mol) (AC-168720010), Diethylamine, 99 % solution ($C_4H_{11}N$, CAS No. 109-89-7, Mw 73.15 g/mol) (AI-A11716-100)

ENVIRONMENTAL CONDITIONS / STABILIZATION
Ambient conditions for operation, temperature: 15 to 35ºC, humidity 20 to 80% RH.

PROCEDURES
Samples should be stored in plastic (HDPE) containers. The containers should be stored dark at a low temperature (+4ºC). Shipment of samples with courier (2 days) at ambient temperature is acceptable.

Methods for measuring alkyl amines and ammonia by GC-MS are based on a derivatization of the amine in the aqueous medium with benzenesulfonyl chloride (BSC). Sample preparation: 10 µL of internal standard methylbutylamine (2g/L) was added to 2 mL of sample. The mixture was basified with 80 µL 10 M aqueous sodium hydroxide solution and 20 µL benzenesulfonyl chloride (BSC) was added. The samples were agitated for 30 min at room temperature. Then another 100 µL of 10 M aqueous sodium hydroxide solution was added (to hydrolyze the excess of derivatization reagent), followed by addition of 500 µL of phosphate buffer solution and 350 µl 18,5% hydrochloride acid. The mixture was agitated again for 30 min at 80˚C. The solutions were cooled to room temperature and 2 mL dichloromethane added. The aqueous solution was discarded, and the organic phase was washed once with 150 µL 0.05 M sodium carbonate solution and dried with sodium sulfate. The solvent was evaporated to a final liquid volume of approx. 100 µL.

Calibration samples should always be analyzed together with the unknown samples in the same analytical series. For control of analytical performance in large sample series, quality control (QC) samples should be included within the analytical series. The QC samples should be spiked with appropriate concentrations of alkyl amines and NH_3 within the calibration range. Method data (instrument parameters) should be stored routinely together with the sample data to verify the methodology used for analysis. Data (sample data and method parameters) should be collected and stored also on a back-up file.

CRITERIA FOR ACCEPTANCE
Acceptance criteria should be applied to chromatographic performance, mass spectrometric performance and the results of the QC samples. Chromatographic criteria: Peak shape should be symmetrical and similar to a calibration standard with comparable concentration, the retention time should be within +/- 0,2 % of the retention time of calibration standard. Mass spectrometric analysis: ion ratio should be within +/- 20%.

DATA TO BE RECORDED / METHOD OF ANALYSIS / DATA PRESENTATION
Raw data must be recorded as separate data files. An intuitive file name structure should be applied to the samples which make it easy and safe to identify analytical series (all the samples analyzed within the same series, together with calibrators and QC samples) as well as the individual unknown samples. Method parameters should be recorded together with raw data, this is normally handled automatically by the instrument software. This is obligatory to secure methodological traceability. It is recommended to calculate concentrations of analyte in unknown samples and QC samples as a batch process. This will allow for more efficient data handling.

UNCERTAINTY OF PROCEDURE

The relative uncertainties of the different steps of the methodological procedure should be estimated and tabulated as an uncertainty budget. The overall instrumental precision measured as % RSD (Relative Standard Deviation) is better than 15 % (n=10) within the measuring range given above.

METHOD DESCRIPTION SCREENING METHOD FOR NITROSAMINES BY GC-MS-NCD

APPROPRIATE IDENTIFICATION
Nitrosamines can be detected and identified by gas chromatography combined with nitrogen chemiluminescence detector (NCD) and mass spectrometry (MS)

SCOPE
Amine solvents, wash water and flue gas samples.

DESCRIPTION OF SAMPLES
Nitrosamines may be detected as by-products in wash water and flue gas samples. These may be dilute aqueous absorption solutions of varying composition, including acids, bases or other constituents in significant amounts.

CONCENTRATION RANGES TO BE DETERMINED
The calibration range for nitrosamines cover a range from 1 to 1 000 mg/L.

INSTRUMENTATION / EQUIPMENT
An Agilent 7890 A gas chromatography – mass spectrometer (GC-MS) system may be used with an Agilent 255 nitrogen chemiluminescence detector (NCD).

Chromatographic conditions:

Column:	DB-WAX: 30m x 250 µm x 0.25 µm
Oven	40 C˚ for 4 min, then 20 C˚/min to 250 C˚ for 7 min
Injection volume	2 µl
Injection temperature	250C˚
Injection mode	Split (25:1)
Transfer line heather	250C˚
Acquisition mode	SCAN
Scan Parameters m/z	50-550
MS source temperature	230C˚
MS quad temperature	150C˚
NCD burner temperature	530C˚
NCD oxidant Flow Rate (sccm)	12
NCD Detector pressure (Torr)	10

Retention time (RT):

NCD-MS	*RT*
N-Nitrosodimethylamine	7.859
N-Nitroso N-Methylethylamine	8.32
N-Nitrosodiethylamine	8.58
N-Nitrosodi-N-Propylamine	9.71
N-Nitroso-n-dibutylamine	10.99
N-Nitrosopiperidine	11.21
N-Nitrosopyrrolidine	11.42
N-Nitrosomorpholine	11.74
N-Nitrosopiperazine	13.38
1.4-Dinitrosopiperazine	16.61
N-Nitrosodiethanolamine	19.99

REFERENCE STANDARDS AND REFERENCE MATERIALS

	Mw g/mol	*Formula*	*CAS No.*	*Prod.nr.*
N-Nitrosodimethylamine	74,08	$C_2H_6N_2O$	62-75-9	EPA 8270
N-Nitroso N-Methylethylamine	88,13	$C_3H_8N_2O$	10595-95-6	“
N-Nitrosodiethylamine	102,14	$C_4H_{10}N_2O$	55-18-5	“
N-Nitrosodi-N-Propylamine	130,19	$C_6H_{14}N_2O$	621-64-7	“
N-Nitroso-n-dibutylamine	158,28	$C_8H_{18}N_2O$	924-16-3	“
N-Nitrosopiperidine	114,15	$C_5H_{10}N_2O$	100-75-4	“
N-Nitrosopyrrolidine	100,12	$C_4H_8N_2O$	930-55-2	“
N-Nitrosomorpholine	116,12	$C_4H_8N_2O_2$	59-89-2	“
N-Nitrosopiperazine	115,13	$C_4H_9N_3O$	5632-47-3	8986.4
1.4-Dinitrosopiperazine	144,13	$C_4H_8N_4O_2$	140-79-4	9019.4-K-ME
N-Nitrosodiethanolamine	134,13	$C_4H_{10}N_2O_3$	1116—54-7	

ENVIRONMENTAL CONDITIONS / STABILIZATION

Ambient conditions for operation, temperature: 15 to 35ºC, humidity 20 to 80% RH.

PROCEDURES

Samples should be contained in plastic (HDPE) containers. The containers should be stored dark at a low temperature (+4ºC). Shipment of samples with courier (2 days) at ambient temperature is acceptable. The calibration samples should always be analyzed together with the unknown samples in the same analytical series with appropriate concentrations of nitrosamines within the calibration range. Method data (instrument parameters) should be stored routinely together with the sample data to verify the methodology used for analysis. Data (sample data and method parameters) should be collected and stored also on a back-up file.

Nitrosamines can be detected by injection of 1:10 dilutions of amine solvents (MEA, PZ and AMP) in the GC-MS-NCD system, and by direct injection of the wash water sample. The high specificity of the NCD-detector for nitrosamines, combined with the versatility of MS introduces a unique possibility to screen for known and unknown nitrosamines. If necessary, this method can be converted to a selected ion monitoring (SIM) method which, combined with a neutral extraction will increase the sensitivity.

CRITERIA FOR ACCEPTANCE

Acceptance criteria should be applied to chromatographic performance of the nitrogen chemiluminescence detector, mass spectrometric performance and the results samples. Chromatographic criteria: Peak shape should be symmetric and similar to a calibration standard with comparable concentration, the retention time should be within +/- 0,2 % of the retention time of calibration standard.

DATA TO BE RECORDED / METHOD OF ANALYSIS / DATA PRESENTATION

Raw data must be recorded as separate data files. An intuitive file name structure should be applied to the samples which make it easy and safe to identify analytical series (all the samples analyzed within the same series, together with calibrators samples) as well as the individual unknown samples. Method parameters should be recorded together with raw data; this is normally handled automatically by the instrument software. This is obligatory to secure methodological traceability. It is recommended to calculate concentrations of analyte in unknown samples as a batch process. This will allow for more efficient data handling.

UNCERTAINTY OF PROCEDURE

The relative uncertainties of the different steps of the methodological procedure should be estimated and tabulated as an uncertainty budget. The overall instrumental precision measured as % RSD (Relative Standard Deviation) is better than 22 % (n=10) for the NCD detector within the measuring range given above.

METHOD DESCRIPTION TOTAL NITROSO COMPOUNDS BY CHEMICAL DENITROSATION USING CuCl/HCl ANALYZED BY GC-NCD

APPROPRIATE IDENTIFICATION

Determination of total N-nitroso compounds (NOC) is performed by chemical denitrosation using CuCl and HCl as described by Wang et al. in J. Agric. Food. Chem., Vol 53, No. 12, 2005. The denitrosation product NO is analyzed with gas chromatography combined with nitrogen chemiluminiscence detection (NCD) by head space technique. By analysis of NOC in MEA, piperazine and AMP based wash water and flue gas amine sorption solution (0.1 M H_2SO_4), a single peak appears in the chromatogram.

SCOPE

Wash water and flue gas samples.

DESCRIPTION OF SAMPLES

Total nitroso compounds may be measured in wash water and flue gas samples. These may be dilute aqueous absorption solutions of varying composition, including acids, bases or other constituents in significant amounts.

CONCENTRATION RANGES TO BE DETERMINED

The calibration range for nitrosamines cover a range from 0.7 to 300 mg/L.

INSTRUMENTATION / EQUIPMENT

An Agilent 7890 A gas chromatography –system may be used with an Agilent 255 nitrogen chemiluminescence detector (NCD).

Chromatographic conditions:

Column:	DB-WAX: 30m x 250 µm x 0.25 µm
Oven	35˚C for 5 min
Injection volume from head space	25 µl
Injection temperature	250˚C
Injection mode	Splitless
Transfer line heather	250˚C
Acquisition mode	SCAN
Scan Parameters m/z	15-200
MS source	230˚C
MS quad	150˚C
NCD temperature	530˚C
NCD oxidant Flow Rate(sccm)	12
NCD Detector pressure (Torr)	10
Retention time (min)	1.40

REFERENCE STANDARDS AND REFERENCE MATERIALS

Different concentration of MIX-standard (containing 9 different nitrosamines) (EPA 8270) and N-Nitrosodimethylamine-standard was used in the denitrosation reaction.

	Mw g/mol	Formula	CAS No.	Prod.nr.
N-Nitrosodimethylamine	74,08	$C_2H_6N_2O$	62-75-9	EPA 8270
N-Nitroso N-Methylethylamine	88,13	$C_3H_8N_2O$	10595-95-6	“
N-Nitrosodiethylamine	102,14	$C_4H_{10}N_2O$	55-18-5	“
N-Nitrosodi-N-Propylamine	130,19	$C_6H_{14}N_2O$	621-64-7	“
N-Nitroso-n-dibutylamine	158,28	$C_8H_{18}N_2O$	924-16-3	“
N-Nitrosopiperidine	114,15	$C_5H_{10}N_2O$	100-75-4	“
N-Nitrosopyrrolidine	100,12	$C_4H_8N_2O$	930-55-2	“
N-Nitrosomorpholine	116,12	$C_4H_8N_2O_2$	59-89-2	“

ENVIRONMENTAL CONDITIONS / STABILIZATION
Ambient conditions for operation, temperature: 15 to 35ºC, humidity 20 to 80% RH.

PROCEDURES
Samples should be contained in plastic (HDPE) containers. The containers should be stored dark at a low temperature (+4ºC). Shipment of samples with courier (2 days) at ambient temperature is acceptable.

Nitrosamines can be determined as total N-nitroso compounds by chemical denitrosation and subsequent GC-NCD detection of evolved NO.

Sample preparation: 100 µL of samples and calibrations standards are added to 900 µL of CuCl in HCl (500 mg CuCl in 10 mL 6 N HCl) in 2 mL vials, and the vials capped immediately. The vials are heated to 70ºC for 30 min.

The calibration samples should always be analyzed together with the unknown samples in the same analytical series with appropriate concentrations of nitrosamines within the calibration range. Method data (instrument parameters) should be stored routinely together with the sample data to verify the methodology used for analysis. Data (sample data and method parameters) should be collected and stored also on a back-up file.

CRITERIA FOR ACCEPTANCE
Acceptance criteria should be applied to chromatographic performance of the nitrogen chemiluminescence detector, mass spectrometric performance and the results samples. Chromatographic criteria: Peak shape should be symmetric and similar to a calibration standard with comparable concentration, the retention time should be within +/- 0.2 % of the retention time of calibration standard.

DATA TO BE RECORDED / METHOD OF ANALYSIS / DATA PRESENTATION
Raw data must be recorded as separate data files. A logic file name structure should be applied to the samples which make it easy and safe to identify analytical series (all the samples analyzed within the same series, together with calibrators samples) as well as the individual unknown samples. Method parameters should be recorded together with raw data;

this is normally handled automatically by the instrument software. This is obligatory to secure methodological traceability. It is recommended to calculate concentrations of analyte in unknown samples as a batch process. This will allow for more efficient data handling.

UNCERTAINTY OF PROCEDURE

The relative uncertainties of the different steps of the methodological procedure should be estimated and tabulated as an uncertainty budget. The overall instrumental precision measured as % RSD (Relative Standard Deviation) is better than 10 % (n=10) within the measuring range given above.

APPENDIX 3:

Validation reports

VALIDATION REPORT FOR N-NITROSODIMETHYLAMINE (NDMA) BY LC-MS-MS-QQQ

SELECTIVITY / SPECIFICITY

NDMA is identified and quantified by a mass spectrometric transition from m/z 75.0 → 43.0. By analysis of NDMA in amine solvent, wash water and flue gas amine sample solution, a single, symmetric peak appears at retention time 2.71 min in the chromatogram. No other compounds have been observed that interfere with the analysis of NDMA with the present methodology.

LINEARITY / MEASURING RANGE

The calibration curves of NDMA are linear over a concentration range from 2,5 µg/L to 5000 µg/L. With d6-NDMA as internal standard, the calibration curves are curvilinear with a R^2 value better than 0.999. With calibration curves that range over three orders of magnitude, concentrations of NDMA can be measured in solutions with a concentration from 10 µg/L up to more than 300 g/L in water by making appropriate dilutions.

ACCURACY

Accuracy can be measured either by comparison of the results from samples analyzed by a reference method (if such a method exists) or by analysis of certified reference material in a relevant matrix. Due to the fact that no reference method or no certified reference material in a relevant matrix exists for NDMA, accuracy has not been determined for NDMA.

PRECISION

Precision has been measured as repeatability by repeated injections from the same sample vial. The repeatability is expressed as %RSD (relative standard deviation). For NDMA, RSD has been determines at three different concentration levels. For 10, 1000 and 5000 µg/L, RSD values of 6.58, 0.64 and 0.90 % were found, respectively.

LIMIT OF DETECTION

Limit of detection (LOD) was determined as the concentration at which the signal-to-noise ratio was larger than 3 (S/N-ratio > 3). For an injection volume of 10µL, the LOD for NDMA was found to be 1 µg/L.

LIMIT OF QUANTIFICATION

Limit of quantification (LOQ) was determined as the concentration at which the signal-to-noise ratio was larger than 10 (S/N-ratio > 10). For an injection volume of 10µL, the LOQ for NDMA was found to be 2,5 µg/L.

ROBUSTNESS / CROSS-SENSITIVITY AGAINST INTERFERENCE

The robustness of the NDMA method against external influences is good. The methodology has been tested and used routinely.

VALIDATION REPORT FOR N-NITROSODIETHYLAMINE (NDEA) BY LC-MS-MS-QQQ

SELECTIVITY / SPECIFICITY

NDEA is identified and quantified by a mass spectrometric transition from m/z 103.1 → 75.0. By analysis of NDEA in amine solvent, wash water and flue gas amine sample solution, a single, symmetric peak appears at retention time 4.56 min in the chromatogram. No other compounds have been observed that interfere with the analysis of NDEA with the present methodology.

LINEARITY / MEASURING RANGE

The calibration curves of NDEA are linear over a concentration range from 1 to 10 000 µg/L. The calibration curves are curvilinear with a R^2 value better than 0.999. With calibration curves that range over three orders of magnitude, concentrations of NDEA can be measured in solutions with a concentration from 1 µg/L up to more than 300 g/L in water by making appropriate dilutions.

ACCURACY

Accuracy can be measured either by comparison of the results from samples analyzed by a reference method (if such a method exists) or by analysis of certified reference material in a relevant matrix. Due to the fact that no reference method or no certified reference material in a relevant matrix exists for NDEA, accuracy has not been determined for NDEA.

PRECISION

Precision has been measured as repeatability by repeated injections from the same sample vial. The repeatability is expressed as %RSD (relative standard deviation). For NDEA, RSD has been determines at three different concentration levels. For 10, 1 000 and 10 000 µg/L, RSD values of 2.42, 0.89 and 0.48 % were found, respectively.

LIMIT OF DETECTION

Limit of detection (LOD) was determined as the concentration at which the signal-to-noise ratio was larger than 3 (S/N-ratio > 3). For an injection volume of 10µL, the LOD for NDEA was found to be 0,5 µg/L.

LIMIT OF QUANTIFICATION

Limit of quantification (LOQ) was determined as the concentration at which the signal-to-noise ratio was larger than 10 (S/N-ratio > 10). For an injection volume of 10 µL, the LOQ for NDEA was found to be 1 µg/L.

ROBUSTNESS / CROSS-SENSITIVITY AGAINST INTERFERENCE

The robustness of the NDEA method against external influences is good. The methodology has been tested and used routinely.

VALIDATION REPORT FOR N-NITROSOMORPHOLINE (NMOR) BY LC-MS-MS-QQQ

SELECTIVITY / SPECIFICITY

NMOR is identified and quantified by a mass spectrometric transition from m/z 117.1 → 45.0. By analysis of NMOR in amine solvent, wash water and flue gas amine sample solution, a single, symmetric peak appears at retention time 2.98 min in the chromatogram. No other compounds have been observed that interfere with the analysis of NMOR with the present methodology.

LINEARITY / MEASURING RANGE

The calibration curves of NMOR are linear over a concentration range from 10 to 10 000 µg/L. The calibration curves are curvilinear with a R^2 value better than 0.999. With calibration curves that range over three orders of magnitude, concentrations of NMOR can be measured in solutions with a concentration from 10 µg/L up to more than 300 g/L in water by making appropriate dilutions.

ACCURACY

Accuracy can be measured either by comparison of the results from samples analyzed by a reference method (if such a method exists) or by analysis of certified reference material in a relevant matrix. Due to the fact that no reference method or no certified reference material in a relevant matrix exists for NMOR, accuracy has not been determined for NMOR.

PRECISION

Precision has been measured as repeatability by repeated injections from the same sample vial. The repeatability is expressed as %RSD (relative standard deviation). For NMOR, RSD has been determines at three different concentration levels. For 10, 1000 and 10 000 µg/L, RSD values of 2.46, 0.67 and 0.58 % were found, respectively.

LIMIT OF DETECTION

Limit of detection (LOD) was determined as the concentration at which the signal-to-noise ratio was larger than 3 (S/N-ratio > 3). For an injection volume of 10µL, the LOD for NMOR was found to be 5 µg/L.

LIMIT OF QUANTIFICATION

Limit of quantification (LOQ) was determined as the concentration at which the signal-to-noise ratio was larger than 10 (S/N-ratio > 10). For an injection volume of 10µL, the LOQ for NMOR was found to be 10 µg/L.

ROBUSTNESS / CROSS-SENSITIVITY AGAINST INTERFERENCE

The robustness of the NMOR method against external influences is good. The methodology has been tested and used routinely.

VALIDATION REPORT FOR N-NITROSOPIPERIDINE (NPIP) BY LC-MS-MS-QQQ

SELECTIVITY / SPECIFICITY

NPIP is identified and quantified by a mass spectrometric transition from m/z 115.1 → 41.1. By analysis of NPIP in amine solvent, wash water and flue gas amine sample solution, a single, symmetric peak appears at retention time 4.82 min in the chromatogram. No other compounds have been observed that interfere with the analysis of NPIP with the present methodology.

LINEARITY / MEASURING RANGE

The calibration curves of NPIP are linear over a concentration range from 0,5 to 10 000 µg/L. The calibration curves are curvilinear with a R^2 value better than 0.999. With calibration curves that range over three orders of magnitude, concentrations of NPIP can be measured in solutions with a concentration from 0,5 µg/L up to more than 300 g/L in water by making appropriate dilutions.

ACCURACY

Accuracy can be measured either by comparison of the results from samples analyzed by a reference method (if such a method exists) or by analysis of certified reference material in a relevant matrix. Due to the fact that no reference method or no certified reference material in a relevant matrix exists for NPIP, accuracy has not been determined for NPIP.

PRECISION

Precision has been measured as repeatability by repeated injections from the same sample vial. The repeatability is expressed as %RSD (relative standard deviation). For NPIP, RSD has been determines at three different concentration levels. For 10, 1000 and 10 000 µg/L, RSD values of 2.67, 0.47 and 0.88 % were found, respectively.

LIMIT OF DETECTION

Limit of detection (LOD) was determined as the concentration at which the signal-to-noise ratio was larger than 3 (S/N-ratio > 3). For an injection volume of 10µL, the LOD for NPIP was found to be 0.25 µg/L.

LIMIT OF QUANTIFICATION

Limit of quantification (LOQ) was determined as the concentration at which the signal-to-noise ratio was larger than 10 (S/N-ratio > 10). For an injection volume of 10µL, the LOQ for NPIP was found to be 0.5 µg/L.

ROBUSTNESS / CROSS-SENSITIVITY AGAINST INTERFERENCE

The robustness of the NPIP method against external influences is good. The methodology has been tested and used routinely.

VALIDATION REPORT FOR N-NITROSODIETHANOLAMINE (NDELA) BY LC-MS-MS-QQQ

SELECTIVITY / SPECIFICITY

NDELA is identified and quantified by a mass spectrometric transition from m/z 135.1 → 74.1. By analysis of NDELA in amine solvent, wash water and flue gas amine sample solution (0.1 M H_2SO_4), a single, symmetric and clean peak appears at retention time 2.27 min in the chromatogram. No other compounds have been observed that interfere with the analysis of NDELA with the present methodology.

LINEARITY / MEASURING RANGE

The calibration curves of NDELA are linear over a concentration range from 1 µg/L to 5000 µg/L. With d8-NDELA as internal standard, the calibration curves are curvilinear with a R^2 value better than 0.999. With calibration curves that range over three orders of magnitude, concentrations of NDELA can be measured in solutions with a concentration from 1 µg/L up to more than 300 g/L in water by making appropriate dilutions.

ACCURACY

Accuracy can be measured either by comparison of the results from samples analyzed by a reference method (if such a method exists) or by analysis of certified reference material in a relevant matrix. Due to the fact that no reference method or no certified reference material in a relevant matrix exists for NDELA, accuracy has not been determined for NDELA.

PRECISION

Precision has been measured as repeatability by repeated injections from the same sample vial. The repeatability is expressed as %RSD (relative standard deviation). For NDELA, RSD has been determines at three different concentration levels. For 10, 1000 and 5000 µg/L, RSD values of 1.81, 0.58 and 0.83 % were found, respectively.

LIMIT OF DETECTION

Limit of detection (LOD) was determined as the concentration at which the signal-to-noise ratio was larger than 3 (S/N-ratio > 3). For an injection volume of 10µL, the LOD for NDELA was found to be 0.5 µg/L.

LIMIT OF QUANTIFICATION

Limit of quantification (LOQ) was determined as the concentration at which the signal-to-noise ratio was larger than 10 (S/N-ratio > 10). For an injection volume of 10µL, the LOQ for NDELA was found to be 1 µg/L.

ROBUSTNESS / CROSS-SENSITIVITY AGAINST INTERFERENCE

The robustness of the NDELA method against external influences is good. The methodology has been tested and used routinely.

VALIDATION REPORT FOR N-NITROSOPIPERAZINE (NPZ) BY LC-MS-MS-QQQ

SELECTIVITY / SPECIFICITY

NPZ is identified and quantified by a mass spectrometric transition from m/z 116.1 → 86.0. By analysis of NPZ in amine solvent, wash water and flue gas amine sample solution, a single, symmetric and clean peak appears at retention time 3.09 min in the chromatogram. No other compounds have been observed that interfere with the analysis of NPZ with the present methodology.

LINEARITY / MEASURING RANGE

The calibration curves of NPZ are linear over a concentration range from 1µg/L to 5000 µg/L. The calibration curves are curvilinear with a R^2 value better than 0.999. With calibration curves that range over four orders of magnitude, concentrations of NPZ can be measured in solutions with a concentration from 0.5 µg/L up to more than 300 g/L in water by making appropriate dilutions.

ACCURACY

Accuracy can be measured either by comparison of the results from samples analyzed by a reference method (if such a method exists) or by analysis of certified reference material in a relevant matrix. Due to the fact that no reference method or no certified reference material in a relevant matrix exists for NPZ, accuracy has not been determined for NPZ.

PRECISION

Precision has been measured as repeatability by repeated injections from the same sample vial. The repeatability is expressed as %RSD (relative standard deviation). For NPZ, RSD has been determines at three different concentration levels. For 10, 1 000 and 10 000 µg/L, RSD values of 0.68, 0.43 and 0.12 % were found, respectively.

LIMIT OF DETECTION

Limit of detection (LOD) was determined as the concentration at which the signal-to-noise ratio was larger than 3 (S/N-ratio > 3). For an injection volume of 10µL, the LOD for NPZ was found to be 0.1 µg/L.

LIMIT OF QUANTIFICATION

Limit of quantification (LOQ) was determined as the concentration at which the signal-to-noise ratio was larger than 10 (S/N-ratio > 10). For an injection volume of 10µL, the LOQ for NPZ was found to be 0.5 µg/L.

ROBUSTNESS / CROSS-SENSITIVITY AGAINST INTERFERENCE

The robustness of the NPZ method against external influences is good. The methodology has been tested and used routinely.

VALIDATION REPORT FOR 1.4-DINITROSOPIPERAZINE (DNPZ) BY LC-MS-MS-QQQ

SELECTIVITY / SPECIFICITY

DNPZ is identified and quantified by a mass spectrometric transition from m/z 145.1 → 56.1. By analysis of DNPZ in PZ based solvents, wash water and flue gas amine sample solution (0.1 M H_2SO_4), a single, symmetric peak appears at retention time 2.67 min in the chromatogram. No other compounds have been observed that interfere with the analysis of DNPZ with the present methodology.

LINEARITY / MEASURING RANGE

The calibration curves of DNPZ are linear over a concentration range from 10 to 10 000 µg/L. The calibration curves are curvilinear with a R^2 value better than 0.999. With calibration curves that range over three orders of magnitude, concentrations of DNPZ can be measured in solutions with a concentration from 10 µg/L up to more than 300 g/L in water by making appropriate dilutions.

ACCURACY

Accuracy can be measured either by comparison of the results from samples analyzed by a reference method (if such a method exists) or by analysis of certified reference material in a relevant matrix. Due to the fact that no reference method or no certified reference material in a relevant matrix exist for DNPZ, accuracy has not been determined for DNPZ.

PRECISION

Precision has been measured as repeatability by repeated injections from the same sample vial. The repeatability is expressed as %RSD (relative standard deviation). For DNPZ, RSD has been determines at three different concentration levels. For 10, 1000 and 10 000 µg/L, RSD values of 2.78, 0.53 and 0.30 % were found, respectively.

LIMIT OF DETECTION

Limit of detection (LOD) was determined as the concentration at which the signal-to-noise ratio was larger than 3 (S/N-ratio > 3). For an injection volume of 10µL, the LOD for DNPZ was found to be 2.5 µg/L.

LIMIT OF QUANTITATION

Limit of quantitation (LOQ) was determined as the concentration at which the signal-to-noise ratio was larger than 10 (S/N-ratio > 10). For an injection volume of 10µL, the LOQ for DNPZ was found to be 5 µg/L.

ROBUSTNESS / CROSS-SENSITIVITY AGAINST INTERFERENCE

The robustness of the DNPZ method against external influences is good. The methodology has been tested and used routinely.

VALIDATION REPORT FOR MONOETHANOLAMINE (MEA) BY LC-MS-MS-QQQ

SELECTIVITY / SPECIFICITY

MEA is identified and quantified by a mass spectrometric transition from m/z 62.1 → 44.2. By analysis of MEA in MEA based solvent, wash water and flue gas amine sample solution (0.1 M H_2SO_4), a single, symmetric and clean peak appears at retention time 2 min in the chromatogram. No other compounds have been observed that interfere with the analysis of MEA with the present methodology.

LINEARITY / MEASURING RANGE

The calibration curves of MEA are linear over a concentration range from 0.050 to 50 mg/L. With d4-MEA as internal standard, the calibration curves are curvilinear with a R^2 value better than 0.999. With calibration curves that range over three orders of magnitude, concentrations of MEA can be measured in solutions with a concentration from 0.05 mg/L up to more than 300 g/L (5M, 30%) in water by making appropriate dilutions.

ACCURACY

Accuracy can be measured either by comparison of the results from samples analyzed by a reference method (if such a method exists) or by analysis of certified reference material in a relevant matrix. Due to the fact that no reference method or no certified reference material in a relevant matrix exists for MEA, accuracy has not been determined for MEA.

PRECISION

Precision has been measured as repeatability by repeated injections from the same sample vial. The repeatability is expressed as %RSD (relative standard deviation). For MEA, RSD has been determines at three different concentration levels. For 0.500, 5 and 50 mg/L, RSD values of 1.18, 0.25 and 0.27 % were found, respectively.

LIMIT OF DETECTION

Limit of detection (LOD) was determined as the concentration at which the signal-to-noise ratio was larger than 3 (S/N-ratio > 3). For an injection volume of 1µL, the LOD for MEA was found to be 0.3 µg/L.

LIMIT OF QUANTIFICATION

Limit of quantification (LOQ) was determined as the concentration at which the signal-to-noise ratio was larger than 10 (S/N-ratio > 10). For an injection volume of 1µL, the LOQ for MEA was found to be 0.6 µg/L.

ROBUSTNESS / CROSS-SENSITIVITY AGAINST INTERFERENCE

The robustness of the MEA method against external influences is good. The methodology has been tested and used routinely. MEA is a strong base (the pH of a 25% solution in water is 12), however, dilution of solvent samples prior to analysis seems to protect the analytical column from exposure to high pH that may cause damage to the silica particles.

VALIDATION REPORT FOR DIETHANOLAMINE (DEA) BY LC-MS-MS-QQQ

SELECTIVITY / SPECIFICITY

DEA is identified and quantified by a mass spectrometric transition from m/z 106.1 → 88.1. By analysis of DEA in MEA based solvent, wash water and flue gas amine sample solution (0.1 M H_2SO_4), a single, symmetric peak appears at retention time 5.09 min in the chromatogram. No other compounds have been observed that interfere with the analysis of DEA with the present methodology.

LINEARITY / MEASURING RANGE

The calibration curves of DEA are linear over a concentration range from 1µg/L to 10 mg/L. With 84-DEA as internal standard, the calibration curves are curvilinear with a R^2 value better than 0.999. With calibration curves that range over three orders of magnitude, concentrations of DEA can be measured in solutions with a concentration from 1µg/L up to more than 300 g/L in water by making appropriate dilutions.

ACCURACY

Accuracy can be measured either by comparison of the results from samples analyzed by a reference method (if such a method exists) or by analysis of certified reference material in a relevant matrix. Due to the fact that no reference method or no certified reference material in a relevant matrix exists for DEA, accuracy has not been determined for DEA.

PRECISION

Precision has been measured as repeatability by repeated injections from the same sample vial. The repeatability is expressed as %RSD (relative standard deviation). For DEA, RSD has been determines at three different concentration levels. For 1, 100 and 10 000 µg/L, RSD values of 2.86, 0.50 and 0.58 % were found, respectively.

LIMIT OF DETECTION

Limit of detection (LOD) was determined as the concentration at which the signal-to-noise ratio was larger than 3 (S/N-ratio > 3). For an injection volume of 5µL, the LOD for DEA was found to be 0.5 µg/L.

LIMIT OF QUANTITATION

Limit of quantitation (LOQ) was determined as the concentration at which the signal-to-noise ratio was larger than 10 (S/N-ratio > 10). For an injection volume of 5µL, the LOQ for DEA was found to be 1 µg/L.

ROBUSTNESS / CROSS-SENSITIVITY AGAINST INTERFERENCE

The robustness of the DEA method against external influences is good. The methodology has been tested and used routinely. DEA is a strong base however, dilution of solvent samples prior to analysis seems to protect the analytical column from exposure to high pH that may cause damage to the silica particles.

VALIDATION REPORT FOR PIPERAZINE (PZ) BY LC-MS-MS-QQQ

SELECTIVITY / SPECIFICITY

PZ is identified and quantified by a mass spectrometric transition from m/z 87.1 → 44.2. By analysis of PZ in PZ based solvent, wash water and flue gas amine sample solution (0.1 M H_2SO_4), a single, symmetric and clean peak appears at retention time 2.2 min in the chromatogram. No other compounds have been observed that interfere with the analysis of PZ with the present methodology.

LINEARITY / MEASURING RANGE

The calibration curves of PZ are linear over a concentration range from 0.086 to 86 mg/L. With d8-PZ as internal standard, the calibration curves are curvilinear with a R^2 value better than 0.999. With calibration curves that range over three orders of magnitude, concentrations of PZ can be measured in solutions with a concentration from 0.086 mg/L up to more than 129 g/L (1.5M) in water by making appropriate dilutions.

ACCURACY

Accuracy can be measured either by comparison of the results from samples analyzed by a reference method (if such a method exists) or by analysis of certified reference material in a relevant matrix. Due to the fact that no reference method or no certified reference material in a relevant matrix exists for PZ, accuracy has not been determined for PZ.

PRECISION

Precision has been measured as repeatability by repeated injections from the same sample vial. The repeatability is expressed as %RSD (relative standard deviation). For PZ, RSD has been determines at three different concentration levels. For 0.86, 8.6 and 86 mg/L, RSD values of 2.45, 2.32 and 2.63 % were found, respectively.

LIMIT OF DETECTION

Limit of detection (LOD) was determined as the concentration at which the signal-to-noise ratio was larger than 3 (S/N-ratio > 3). For an injection volume of 1µL, the LOD for PZ was found to be 0.4 µg/L.

LIMIT OF QUANTIFICATION

Limit of quantification (LOQ) was determined as the concentration at which the signal-to-noise ratio was larger than 10 (S/N-ratio > 10). For an injection volume of 1µL, the LOQ for PZ was found to be 0,9 µg/L.

ROBUSTNESS / CROSS-SENSITIVITY AGAINST INTERFERENCE

The robustness of the PZ method against external influences is good. The methodology has been tested and used routinely. PZ is a strong base, however, dilution of solvent samples prior to analysis seems to protect the analytical column from exposure to high pH that may cause damage to the silica particles.

VALIDATION REPORT FOR 2-AMINO-2-METHYL-1-PROPANOL (AMP) BY LC-MS-MS-QQQ

SELECTIVITY / SPECIFICITY

AMP is identified and quantified by a mass spectrometric transition from m/z 90.1 → 55.2. By analysis of AMP in AMP based solvent, wash water and flue gas amine sample solution (0.1 M H_2SO_4), a single, symmetric peak appears at retention time 2.56 min in the chromatogram. No other compounds have been observed that interfere with the analysis of AMP with the present methodology.

LINEARITY / MEASURING RANGE

The calibration curves of AMP are linear over a concentration range from 0.089 to 89 mg/L. The calibration curves are curvilinear with a R^2 value better than 0.999. With calibration curves that range over three orders of magnitude, concentrations of AMP can be measured in solutions with a concentration from 0.089 mg/L up to more than 267 g/L (3M) in water by making appropriate dilutions.

ACCURACY

Accuracy can be measured either by comparison of the results from samples analyzed by a reference method (if such a method exists) or by analysis of certified reference material in a relevant matrix. Due to the fact that no reference method or no certified reference material in a relevant matrix exists for AMP, accuracy has not been determined for AMP.

PRECISION

Precision has been measured as repeatability by repeated injections from the same sample vial. The repeatability is expressed as %RSD (relative standard deviation). For AMP, RSD has been determines at three different concentration levels. For 0.89, 8.9 and 89 mg/L, RSD values of 1.13, 1.69 and 2.86 % were found, respectively.

LIMIT OF DETECTION

Limit of detection (LOD) was determined as the concentration at which the signal-to-noise ratio was larger than 3 (S/N-ratio > 3). For an injection volume of 1µL, the LOD for AMP was found to be 0.4 µg/L.

LIMIT OF QUANTIFICATION

Limit of quantification (LOQ) was determined as the concentration at which the signal-to-noise ratio was larger than 10 (S/N-ratio > 10). For an injection volume of 1µL, the LOQ for AMP was found to be 0.9 µg/L.

ROBUSTNESS / CROSS-SENSITIVITY AGAINST INTERFERENCE

The robustness of the AMP method against external influences is good. The methodology has been tested and used routinely.

VALIDATION REPORT FOR N-METHYLDIETHANOLAMINE (MDEA) BY LC-MS-MS-QQQ

SELECTIVITY / SPECIFICITY

MDEA is identified and quantified by a mass spectrometric transition from m/z 120.1 → 58.2. By analysis of MDEA in MDEA solvent, wash water and flue gas amine sample solution (0.1 M H_2SO_4), a single, symmetric peak appears at retention time 2.37 min in the chromatogram. No other compounds have been observed that interfere with the analysis of MDEA with the present methodology.

LINEARITY / MEASURING RANGE

The calibration curves of MDEA are linear over a concentration range from 1 µg/L to 120 mg/L. The calibration curves are curvilinear with a R^2 value better than 0.999. With calibration curves that range over three orders of magnitude, concentrations of MDEA can be measured in solutions with a concentration from 1 µg/L up to more than 300 g/L (5M, 30%) in water by making appropriate dilutions.

ACCURACY

Accuracy can be measured either by comparison of the results from samples analyzed by a reference method (if such a method exists) or by analysis of certified reference material in a relevant matrix. Due to the fact that no reference method or no certified reference material in a relevant matrix exists for MDEA, accuracy has not been determined for MDEA.

PRECISION

Precision has been measured as repeatability by repeated injections from the same sample vial. The repeatability is expressed as %RSD (relative standard deviation). For MDEA, RSD has been determines at two different concentration levels. For 119 µg/L and 119 mg/L, RSD values of 0.20 and 0.45 % were found, respectively.

LIMIT OF DETECTION

Limit of detection (LOD) was determined as the concentration at which the signal-to-noise ratio was larger than 3 (S/N-ratio > 3). For an injection volume of 2 µL, the LOD for MDEA was found to be 0.6 µg/L.

LIMIT OF QUANTITATION

Limit of detection (LOQ) was determined as the concentration at which the signal-to-noise ratio was larger than 10 (S/N-ratio > 10). For an injection volume of 2 µL, the LOQ for MDEA was found to be 1.2 µg/L.

ROBUSTNESS / CROSS-SENSITIVITY AGAINST INTERFERENCE

The robustness of the MDEA method against external influences is good. The methodology has been tested and used routinely. MDEA is a base, however, dilution of solvent samples prior to analysis seems to protect the analytical column from exposure to high pH that may cause damage to the silica particles.

VALIDATION REPORT FOR 1.2–DIAMINOETHANE (EDA) BY LC-MS-MS-QQQ

SELECTIVITY / SPECIFICITY

EDA is identified and quantified by a mass spectrometric transition from m/z 61.1 → 44.1. By analysis of EDA in EDA based solvent, wash water and flue gas amine sample solution (0.1 M H_2SO_4), a single, symmetric and clean peak appears at retention time 2.2 min in the chromatogram. No other compounds have been observed that interfere with the analysis of EDA with the present methodology.

LINEARITY / MEASURING RANGE

The calibration curves of EDA are linear over a concentration range from a level yet to be determined to 50 mg/L. The calibration curves are curvilinear with a R^2 value better than 0.999. With calibration curves that range over three orders of magnitude, concentrations of EDA can be measured in solutions with a concentration from a level yet to be determined up to more than 300 g/L (5M, 30%) in water by making appropriate dilutions.

ACCURACY

Yet to be determined.

PRECISION

Yet to be determined.

LIMIT OF DETECTION

Yet to be determined.

LIMIT OF QUANTIFICATION

Yet to be determined.

ROBUSTNESS / CROSS-SENSITIVITY AGAINST INTERFERENCE

Yet to be determined.

VALIDATION REPORT FOR FORMAMIDE BY LC-MS-MS-QQQ

SELECTIVITY / SPECIFICITY

Formamide is identified and quantified by a mass spectrometric transition from m/z 46.1 → 46.1. By analysis of formamide in formamide based solvent, wash water and flue gas amine sample solution (0.1 M H_2SO_4), a single, symmetric peak appears at retention time 2.49 min in the chromatogram. No other compounds have been observed that interfere with the analysis of formamide with the present methodology.

LINEARITY / MEASURING RANGE

The calibration curves of formamide are linear over a concentration range from 10 to 10 000 µg/L. The calibration curves are curvilinear with a R^2 value better than 0.999. With calibration curves that range over three orders of magnitude, concentrations of formamide can be measured in solutions with a concentration from 10 µg/L up to more than 300 g/L in water by making appropriate dilutions.

ACCURACY

Accuracy can be measured either by comparison of the results from samples analyzed by a reference method (if such a method exists) or by analysis of certified reference material in a relevant matrix. Due to the fact that no reference method or no certified reference material in a relevant matrix exists for formamide, accuracy has not been determined for formamide.

PRECISION

Precision has been measured as repeatability by repeated injections from the same sample vial. The repeatability is expressed as %RSD (relative standard deviation). For formamide, RSD has been determines at two different concentration levels. For 100 and 1000 µg/L, RSD values of 2.44 and 0.58 % were found, respectively.

LIMIT OF DETECTION

Limit of detection (LOD) was determined as the concentration at which the signal-to-noise ratio was larger than 3 (S/N-ratio > 3). For an injection volume of 1µL, the LOD for formamide was found to be 5 µg/L.

LIMIT OF QUANTIFICATION

Limit of quantification (LOQ) was determined as the concentration at which the signal-to-noise ratio was larger than 10 (S/N-ratio > 10). For an injection volume of 5µL, the LOQ for formamide was found to be 10 µg/L

ROBUSTNESS / CROSS-SENSITIVITY AGAINST INTERFERENCE

The robustness of the formamide method against external influences is not well known as the method is newly developed and has not been used routinely for a long time.

VALIDATION REPORT FOR ACETAMIDE BY LC-MS-MS-QQQ

SELECTIVITY / SPECIFICITY

Acetamide is identified and quantified by a mass spectrometric transition from m/z 60.0 → 43.0. By analysis of acetamide in amine solvents, wash water and flue gas amine sample solution (0.1 M H_2SO_4), a single, symmetric peak appears at retention time 3.34 min in the chromatogram. No other compounds have been observed that interfere with the analysis of acetamide with the present methodology.

LINEARITY / MEASURING RANGE

The calibration curves of acetamide are linear over a concentration range from 10 to 10000 µg/L. With d5-acetamide as internal standard, the calibration curves are curvilinear with a R^2 value better than 0.999. With calibration curves that range over three orders of magnitude, concentrations of acetamide can be measured in solutions with a concentration from 10 µg/L up to more than 300 g/L in water by making appropriate dilutions.

ACCURACY

Accuracy can be measured either by comparison of the results from samples analyzed by a reference method (if such a method exists) or by analysis of certified reference material in a relevant matrix. Due to the fact that no reference method or no certified reference material in a relevant matrix exists for acetamide, accuracy has not been determined for acetamide.

PRECISION

Precision has been measured as repeatability by repeated injections from the same sample vial. The repeatability is expressed as %RSD (relative standard deviation). For acetamide, RSD has been determines at two different concentration levels. For 100 and 1000 µg/L, RSD values of 2.22 and 0.50 % were found, respectively.

LIMIT OF DETECTION

Limit of detection (LOD) was determined as the concentration at which the signal-to-noise ratio was larger than 3 (S/N-ratio > 3). For an injection volume of 5µL, the LOD for acetamide was found to be 5 µg/L.

LIMIT OF QUANTITATION

Limit of quantitation (LOQ) was determined as the concentration at which the signal-to-noise ratio was larger than 10 (S/N-ratio > 10). For an injection volume of 5µL, the LOQ for acetamide was found to be 10 µg/L.

ROBUSTNESS / CROSS-SENSITIVITY AGAINST INTERFERENCE

The robustness of the acetamide method against external influences is not well known as the methodology is newly developed and little experience exists from routine analysis..

VALIDATION REPORT FOR FORMALDEHYDE BY LC-MS-MS-QQQ

SELECTIVITY / SPECIFICITY

Formaldehyde-DNPH is identified and quantified by a mass spectrometric transition from m/z 209,1 → 46.0 and 209,1 → 120.8. By analysis of formaldehyde in amine solvent, wash water and flue gas amine sample solution (0.1 M H_2SO_4), a single, symmetric peak appears at retention time 3.08 min in the chromatogram. No other compounds have been observed that interfere with the analysis of formaldehyde with the present methodology.

LINEARITY / MEASURING RANGE

The calibration curves of formaldehyde are linear over a concentration range from 10 to 10 000 µg/L. The calibration curves are curvilinear (quadratic) with a R^2 value better than 0.999. With calibration curves that range over three orders of magnitude, concentrations of formaldehyde can be measured in solutions with a concentration from 10 µg/L up to more than 300 g/L in water by making appropriate dilutions.

ACCURACY

Accuracy can be measured either by comparison of the results from samples analyzed by a reference method (if such a method exists) or by analysis of certified reference material in a relevant matrix. Due to the fact that no reference method or no certified reference material in a relevant matrix exists for formaldehyde, accuracy has not been determined for formaldehyde.

PRECISION

Precision has been measured as repeatability by repeated injections from the same sample vial. The repeatability is expressed as %RSD (relative standard deviation). For formaldehyde, RSD has been determined at two different concentration levels. For 100 µg/L and 1 000 µg/L, RSD values of 1.66 and 1.46 % were found, respectively.

LIMIT OF DETECTION

Limit of detection (LOD) was determined as the concentration at which the signal-to-noise ratio was larger than 3 (S/N-ratio > 3). For an injection volume of 1µL, the LOD for formaldehyde was found to be 5 µg/L.

LIMIT OF QUANTIFICATION

Limit of quantification (LOQ) was determined as the concentration at which the signal-to-noise ratio was larger than 10 (S/N-ratio > 10). For an injection volume of 1µL, the LOQ for formaldehyde was found to be 10 µg/L.

ROBUSTNESS / CROSS-SENSITIVITY AGAINST INTERFERENCE

The robustness of the formaldehyde-DNPH method against external influences is not well known as the method is newly developed and has not been used routinely for a long time. Careful control of temperature during the derivatization step must be ensured.

VALIDATION REPORT FOR ACETALDEHYDE BY LC-MS-MS-QQQ

SELECTIVITY / SPECIFICITY

Acetaldehyde-DNPH is identified and quantified by a mass spectrometric transition from m/z 223,1 → 46.0 and 223,1 → 163.0. By analysis of acetaldehyde in amine solvents, wash water and flue gas amine sample solution, a single, symmetric peak appears at retention time 4.2 min in the chromatogram. No other compounds have been observed that interfere with the analysis of formaldehyde with the present methodology.

LINEARITY / MEASURING RANGE

The calibration curves of acetaldehyde are linear over a concentration range from 10 to 10 000 µg/L. The calibration curves are curvilinear with a R^2 value better than 0.999. With calibration curves that range over three orders of magnitude, concentrations of formaldehyde can be measured in solutions with a concentration from 0.05 mg/L up to more than 300 g/L in water by making appropriate dilutions.

ACCURACY

Accuracy can be measured either by comparison of the results from samples analyzed by a reference method (if such a method exists) or by analysis of certified reference material in a relevant matrix. Due to the fact that no reference method or no certified reference material in a relevant matrix exists for acetaldehyde, accuracy has not been determined for acetaldehyde.

PRECISION

Precision has been measured as repeatability by repeated injections from the same sample vial. The repeatability is expressed as %RSD (relative standard deviation). For acetaldehyde, RSD has been determined at two different concentration levels. For 100 µg/L and 1 000 µg/L, RSD values of 1.20 and 1.52 % were found, respectively.

LIMIT OF DETECTION

Limit of detection (LOD) was determined as the concentration at which the signal-to-noise ratio was larger than 3 (S/N-ratio > 3). For an injection volume of 1µL, the LOD for acetaldehyde was found to be 5 µg/L.

LIMIT OF QUANTIFICATION

Limit of quantification (LOQ) was determined as the concentration at which the signal-to-noise ratio was larger than 10 (S/N-ratio > 10). For an injection volume of 1µL, the LOQ for acetaldehyde was found to be 10 µg/L.

ROBUSTNESS / CROSS-SENSITIVITY AGAINST INTERFERENCE

The robustness of the acetaldehyde-DNPH method against external influences is not well known as the method is newly developed and has not been used routinely for a long time. Careful control of temperature during the derivatization step must be ensured.

VALIDATION REPORT FOR AMMONIA (NH_3) BY GC-MS

SELECTIVITY / SPECIFICITY

NH_3 is converted into a suitable derivative with benzenesulfonyl chloride (BSC), identified and quantified by mass spectrometry at m/z 157. By analysis of NH_3 in wash water and flue gas amine sample solution (0.1 M H_2SO_4), a single, symmetric and clean peak appears at retention time 15.55 min in the chromatogram. No other compounds have been observed that interfere with the analysis of NH_3 with the present methodology.

LINEARITY / MEASURING RANGE

The calibration curves of NH_3 are linear over a concentration range from 1 to 100 mg/L. The calibration curves are curvilinear with a R^2 value = 0.9998. With calibration curves that range over three orders of magnitude, concentrations of NH_3 can be measured in solutions with a concentration from 1 mg/L up to 100 mg/L.

ACCURACY

Accuracy can be measured either by comparison of the results from samples analyzed by a reference method (if such a method exists) or by analysis of certified reference material in a relevant matrix. Due to the fact that no reference method or no certified reference material in a relevant matrix exists for NH_3, accuracy has not been determined for NH_3.

PRECISION

Precision has been measured as repeatability by repeated injections from the same sample vial. The repeatability is expressed as %RSD (relative standard deviation). For NH_3, RSD has been determines at three different concentration levels. For 10, 100 and 1000 mg/L, RSD values of 9.12 and 15 % were found, respectively.

LIMIT OF DETECTION

Limit of detection (LOD) was determined as the concentration at which the signal-to-noise ratio was larger than 3 (S/N-ratio > 3). The derivative formed with BSC is extracted and the solution concentrated to a factor x20.For an injection volume of 2 µL, the LOD for NH_3 was found to be 1 mg/L.

ROBUSTNESS / CROSS-SENSITIVITY AGAINST INTERFERENCE

The robustness of the NH_3 method against external influences is good. The methodology has been tested and used routinely. The methodology is not primarily developed for analysis in amine solvents.

VALIDATION REPORT FOR METHYLAMINE BY GC-MS

SELECTIVITY / SPECIFICITY

Methylamine is converted into a suitable derivative with benzenesulfonyl chloride (BSC), identified and quantified by mass spectrometry at m/z 171. By analysis of methylamine in wash water and flue gas amine sample solution (0.1 M H_2SO_4), a single, symmetric peak appears at retention time 15.8 min in the chromatogram. No other compounds have been observed that interfere with the analysis of methylamine with the present methodology.

LINEARITY / MEASURING RANGE

The calibration curves of methylamine are linear over a concentration range from 0.001 to 1 µg/L. The calibration curves are curvilinear with a R^2 value = 0.998. With calibration curves that range over three orders of magnitude, concentrations of methylamine can be measured in solutions with a concentration from 0.001 µg/L up to 1 µg/L.

ACCURACY

Accuracy can be measured either by comparison of the results from samples analyzed by a reference method (if such a method exists) or by analysis of certified reference material in a relevant matrix. Due to the fact that no reference method or no certified reference material in a relevant matrix exists for methylamine, accuracy has not been determined for methylamine.

PRECISION

Precision has been measured as repeatability by repeated injections from the same sample vial. The repeatability is expressed as %RSD (relative standard deviation). For methylamine, RSD has been determines at three different concentration levels. For 0.01, 0.1 and 1 µg/L, RSD values of 5.9, 10 and 10 % were found, respectively.

LIMIT OF DETECTION

Limit of detection (LOD) was determined as the concentration at which the signal-to-noise ratio was larger than 3 (S/N-ratio > 3). The derivative formed with BSC is extracted and the solution concentrated to a factor x20.For an injection volume of 2 µL, the LOD for methylamine was found to be 1 µg/L.

ROBUSTNESS / CROSS-SENSITIVITY AGAINST INTERFERENCE

The robustness of the methylamine method against external influences is good. The methodology has been tested and used routinely. The methodology is not primarily developed for analysis in amine solvents.

VALIDATION REPORT FOR ETHYLAMINE BY GC-MS

SELECTIVITY / SPECIFICITY

Ethylamine is converted into a suitable derivative with benzenesulfonyl chloride (BSC), identified and quantified by mass spectrometry at m/z 170. By analysis of ethylamine in wash water and flue gas amine sample solution (0.1 M H_2SO_4), a single, symmetric peak appears at retention time 16.51 min in the chromatogram. No other compounds have been observed that interfere with the analysis of ethylamine with the present methodology.

LINEARITY / MEASURING RANGE

The calibration curves of ethylamine are linear over a concentration range from 0.001 to 1 µg/L. The calibration curves are curvilinear with a R^2 value = 0.999. With calibration curves that range over three orders of magnitude, concentrations of ethylamine can be measured in solutions with a concentration from 0.001 µg/L up to 1 µg/L.

ACCURACY

Accuracy can be measured either by comparison of the results from samples analyzed by a reference method (if such a method exists) or by analysis of certified reference material in a relevant matrix. Due to the fact that no reference method or no certified reference material in a relevant matrix exists for ethylamine, accuracy has not been determined for ethylamine.

PRECISION

Precision has been measured as repeatability by repeated injections from the same sample vial. The repeatability is expressed as %RSD (relative standard deviation). For ethylamine, RSD has been determines at three different concentration levels. For 0.01, 0.1 and 1 µg/L, RSD values of 8, 12 and 11 % were found, respectively.

LIMIT OF DETECTION

Limit of detection (LOD) was determined as the concentration at which the signal-to-noise ratio was larger than 3 (S/N-ratio > 3). The derivative formed with BSC is extracted and the solution concentrated to a factor x20.For an injection volume of 2 µL, the LOD for ethylamine was found to be 1 µg/L.

ROBUSTNESS / CROSS-SENSITIVITY AGAINST INTERFERENCE

The robustness of the ethylamine method against external influences is good. The methodology has been tested and used routinely. The methodology is not primarily developed for analysis in amine solvents.

VALIDATION REPORT FOR DIMETHYLAMINE BY GC-MS

SELECTIVITY / SPECIFICITY

Dimethylamine is converted into a suitable derivative with benzenesulfonyl chloride (BSC), identified and quantified by mass spectrometry at m/z 185. By analysis of dimethylamine in wash water and flue gas amine sample solution (0.1 M H_2SO_4), a single, symmetric peak appears at retention time 15.65 min in the chromatogram. No other compounds have been observed that interfere with the analysis of dimethylamine with the present methodology.

LINEARITY / MEASURING RANGE

The calibration curves of dimethylamine are linear over a concentration range from 0.001 to 1 µg/L. The calibration curves are curvilinear with a R^2 value = 0.998. With calibration curves that range over three orders of magnitude, concentrations of dimethylamine can be measured in solutions with a concentration from 0.001 µg/L up to 1 µg/L.

ACCURACY

Accuracy can be measured either by comparison of the results from samples analyzed by a reference method (if such a method exists) or by analysis of certified reference material in a relevant matrix. Due to the fact that no reference method or no certified reference material in a relevant matrix exists for dimethylamine, accuracy has not been determined for dimethylamine.

PRECISION

Precision has been measured as repeatability by repeated injections from the same sample vial. The repeatability is expressed as %RSD (relative standard deviation). For dimethylamine, RSD has been determines at three different concentration levels. For 0.01, 0.1 and 1 µg/L, RSD values of 6, 10 and 10 % were found, respectively.

LIMIT OF DETECTION

Limit of detection (LOD) was determined as the concentration at which the signal-to-noise ratio was larger than 3 (S/N-ratio > 3). The derivative formed with BSC, is extracted and the solution concentrated to a factor x20.For an injection volume of 2 µL, the LOD for dimethylamine was found to be 1 µg/L.

ROBUSTNESS / CROSS-SENSITIVITY AGAINST INTERFERENCE

The robustness of the dimethylamine method against external influences is good. The methodology has been tested and used routinely. The methodology is not primarily developed for analysis in amine solvents.

VALIDATION REPORT FOR DIETHYLAMINE BY GC-MS

SELECTIVITY / SPECIFICITY

Diethylamine is converted into a suitable derivative with benzenesulfonyl chloride (BSC), identified and quantified by mass spectrometry at m/z 198. By analysis of diethylamine in wash water and flue gas amine sample solution (0.1 M H_2SO_4), a single, symmetric and clean peak appears at retention time 17.81 min in the chromatogram. No other compounds have been observed that interfere with the analysis of diethylamine with the present methodology.

LINEARITY / MEASURING RANGE

The calibration curves of diethylamine are linear over a concentration range from 0.001 to 1 µg/L. The calibration curves are curvilinear with a R^2 value = 0.999. With calibration curves that range over three orders of magnitude, concentrations of diethylamine can be measured in solutions with a concentration from 0.001 µg/L up to 1 µg/L.

ACCURACY

Accuracy can be measured either by comparison of the results from samples analyzed by a reference method (if such a method exists) or by analysis of certified reference material in a relevant matrix. Due to the fact that no reference method or no certified reference material in a relevant matrix exists for diethylamine, accuracy has not been determined for diethylamine.

PRECISION

Precision has been measured as repeatability by repeated injections from the same sample vial. The repeatability is expressed as %RSD (relative standard deviation). For diethylamine, RSD has been determined at three different concentration levels. For 0.01, 0.1 and 1 µg/L, RSD values of 8, 9 and 10 % were found, respectively.

LIMIT OF DETECTION

Limit of detection (LOD) was determined as the concentration at which the signal-to-noise ratio was larger than 3 (S/N-ratio > 3). The derivative formed with BSC is extracted and the solution concentrated to a factor x20.For an injection volume of 2 µL, the LOD for diethylamine was found to be 1 µg/L.

ROBUSTNESS / CROSS-SENSITIVITY AGAINST INTERFERENCE

The robustness of the diethylamine method against external influences is good. The methodology has been tested and used routinely. The methodology is not primarily developed for analysis in amine solvents.

VALIDATION REPORT FOR SCREENING METHOD FOR NITROSAMINES BY GC-NCD AND GC-MS

SELECTIVITY / SPECIFICITY

Nitrosamines are identified by a gas chromatography combined nitrogen chemiluminiscence detector (NCD) a mass spectrometric (MS). By analysis of nitrosamines in MEA, piperazine and AMP based solvent, wash water and flue gas amine sample solution, a single symmetric peak appears in the chromatogram (table 1). No other compounds have been observed that interfere with the scan analysis of nitrosamines with the present methodology. Retention time, linearity, measuring range, and limit of detection are decried in the table below.

Table 1:

NCD	RT	LINEARITY	MEASURING RANGE	PRECISION 100 mg/l	LIMIT OF DETECTION
N-Nitrosodimethylamine	7.86	R^2=1,000	1-1000 mg/L	21	1 mg/L
N-Nitroso-Methylethylamine	8.32	R^2= 0,998	1-1000 mg/L	18	1 mg/L
N-Nitrosodiethylamine	8.58	R^2= 0,999	1-1000 mg/L	20	1 mg/L
N-Nitrosodi-Propylamine	9.71	R^2= 0,997	1-1000 mg/L	22	1 mg/L
N-Nitroso-n-dibutylamine	10.99	R^2= 0,995	1-1000 mg/L	21	1 mg/L
N-Nitrosopiperidine	11.21	R^2= 0,999	1-1000 mg/L	22	1 mg/L
N-Nitrosopyrrolidine	11.42	R^2=1,000	1-1000 mg/L	22	1 mg/L
N-Nitrosomorpholine	11.74	R^2= 0,994	1-1000 mg/L	20	1 mg/L
N-Nitrosopiperazine	13.38	R^2= 0,998	1-1000 mg/L	20	1 mg/L
N-Nitroso-Methylethylamine	16,61	R^2= 0,998	1-1000 mg/L	20	1 mg/L
N-Nitrosodiethanolamine	19,99	R^2= 0,998	10-1000 mg/L	24	10 mg/L

LINEARITY: Linear over the concentration range covered by the calibration curves
MEASURING RANGE: Three orders of magnitude
PRECISION: Precision has been measured as repeatability by repeated injections from the same sample vial. The repeatability is expressed as %RSD (relative standard deviation).
LIMIT OF DETECTION: Limit of detection (LOD) was determined as the concentration at which the signal-to-noise ratio was larger than 3 (S/N-ratio > 3).

ACCURACY

Accuracy can be measured either by comparison of the results from samples analyzed by a reference method (if such a method exists) or by analysis of certified reference material in a relevant matrix. Due to the fact that no reference method or no certified reference material in a relevant matrix exists for ethylamine, accuracy has not been determined for ethylamine.

ROBUSTNESS / CROSS-SENSITIVITY AGAINST INTERFERENCE

The robustness of the ethylamine method against external influences is good. The methodology has been tested and used routinely.

VALIDATION REPORT DETERMINATION OF TOTAL NITROSO COMPOUNDS BY CHEMICAL DENITROSATION USING CuCl BY GC-NCD

SELECTIVITY / SPECIFICITY

Determination of total nitroso compounds (NOC) are identified by chemical denitrosation using CuCl. The denitrosation product NO is analyzed with a gas chromatography combined with nitrogen chemiluminiscence detection (NCD) by head space technique. By analysis of NOC in MEA , piperazine and AMP based solvent, wash water and flue gas amine sample solution (0.1 M H2SO4), single, symmetric peaks appears in the chromatogram

LINEARITY / MEASURING RANGE

The calibration curves of NOC are linear over a concentration range from 0.7 to 33 mg/L with chemical denitosation of nitrosodimethylamine. The calibration curves are curvilinear with a R^2 value 0.998. Concentrations of NOC can be measured in solutions with a concentration from 0.7 mg/L up to more than 33 mg/L.

ACCURACY

Accuracy can be measured either by comparison of the results from samples analyzed by a reference method (if such a method exists) or by analysis of certified reference material in a relevant matrix. Due to the fact that no reference method or no certified reference material in a relevant matrix exists for NOC, accuracy has not been determined for NOC.

PRECISION

Precision has been measured as repeatability by repeated injections from the same sample vial. The repeatability is expressed as %RSD (relative standard deviation). A precision better than 10% RSD has been determined for the whole concentration range from 0.7 to 0.33 mg/L.

LIMIT OF DETECTION

Limit of detection (LOD) was determined as the concentration at which the signal-to-noise ratio was larger than 3 (S/N-ratio > 3). For an injection volume of 25 µL, the LOD for NOC was found to be 0.7 µg/L.

ACCURACY

Accuracy can be measured either by comparison of the results from samples analyzed by a reference method (if such a method exists) or by analysis of certified reference material in a relevant matrix. Due to the fact that no reference method or no certified reference material in a relevant matrix exists for NOC, accuracy has not been determined for ethylamine.

ROBUSTNESS / CROSS-SENSITIVITY AGAINST INTERFERENCE

The robustness of the CuCl /HCl method against external influences is not known. The methodology is newly developed and has not been used in routine analyses.

APPENDIX 4:

Stability studies

Table 1. Results from stability studies with nitrosamines at concentration 2000 µg/L and duration 50 days. Individual sample conditions are given in table.

Analyte	2000 µg/L Room temp. – light exposed 50 days	2000 µg/L Room temp. 50 days	2000 µg/L +4°C 50 days	2000 µg/L - 20°C 50 days	Unit
Dinitrosopiperazine	1589	2075	2040	2038	**µg/L**
Nitrosopiperazine	1794	2128	2040	2049	**µg/L**
Nitrosodiethanolamine	1803	2048	2024	2055	**µg/L**
Nitrosodimethylamine	1999	2055	2041	1980	**µg/L**
Nitrosomorpholine	1813	2100	2108	2061	**µg/L**
Nitrosopyrrolidine	2030	2174	2057	2059	**µg/L**
Nitroso-N-Methylethylamine	2010	2064	2059	2030	**µg/L**
Nitrosodiethylamine	1967	2023	2077	2033	**µg/L**
Nitrosopiperidine	1951	2170	2107	2087	**µg/L**
Nitroso-N-propylamine	1962	2020	2060	2104	**µg/L**
Nitroso-n-butylamine	2043	2069	2265	2250	**µg/L**

Table 2. Results from stability studies with nitrosamines at concentration 2000 µg/L and duration 68 days. Individual sample conditions are given in table.

Analyte	2000 µg/L Room temp. – light exposed 68 days	2000 µg/L Room temp. 68 days	2000 µg/L +4°C 68 days	2000 µg/L - 20°C 68 days	Unit
Dinitrosopiperazine	1293	2137	2080	2074	**µg/L**
Nitrosopiperazine	1583	2142	2081	2089	**µg/L**
Nitrosodiethanolamine	1640	2067	1994	1911	**µg/L**
Nitrosodimethylamine	1884	2037	2016	1938	**µg/L**
Nitrosomorpholine	1642	2147	2101	1935	**µg/L**
Nitrosopyrrolidine	1961	2163	2205	2001	**µg/L**
Nitroso-N-Methylethylamine	1881	2032	2038	1948	**µg/L**
Nitrosodiethylamine	1865	2011	2026	2011	**µg/L**
Nitrosopiperidine	1794	2103	2071	1919	**µg/L**
Nitroso-N-propylamine	1838	1964	2074	2056	**µg/L**
Nitroso-n-butylamine	1729	1938	2207	2168	**µg/L**

Table 3. Results from stability studies with nitrosamines at concentration 200 µg/L and duration 18 days, stored in glass vials. Individual sample conditions are given in table.

Stored in glass vials						
Analyte	**200 µg/L Room temp. – light exposed 18 days**	**200 µg/L Room temp. 18 days**	**200 µg/L 50°C 18 days**	**200 µg/L +4°C 18 days**	**200 µg/L - 20°C 18 days**	**Unit**
Dinitrosopiperazine	198	205	199	209	207	**µg/L**
Nitrosopiperazine	200	205	210	204	205	**µg/L**
Nitrosodiethanolamine	172	190	180	187	194	**µg/L**
Nitrosodimethylamine	198	198	199	201	180	**µg/L**
Nitrosomorpholine	194	203	200	203	195	**µg/L**
Nitrosopyrrolidine	199	212	203	215	212	**µg/L**
Nitroso-N-Methylethylamine	194	197	198	200	183	**µg/L**
Nitrosodiethylamine	194	197	196	201	181	**µg/L**
Nitrosopiperidine	196	197	200	199	189	**µg/L**
Nitroso-N-propylamine	198	201	198	205	185	**µg/L**
Nitroso-N-butylamine	201	204	192	208	194	**µg/L**

Table 4. Results from stability studies with nitrosamines at concentration 200 µg/L and duration 18 days, stored in HDPE vials. Individual sample conditions are given in table.

Stored in HDPE vials						
Analyte	**200 µg/L Room temp. – light exposed 18 days**	**200 µg/L Room temp. 18 days**	**200 µg/L 50°C 18 days**	**200 µg/L +4°C 18 days**	**200 µg/L - 20°C 18 days**	**Unit**
Dinitrosopiperazine	188	201	203	208	220	**µg/L**
Nitrosopiperazine	195	202	213	204	225	**µg/L**
Nitrosodiethanolamine	205	206	216	197	215	**µg/L**
Nitrosodimethylamine	195	195	198	198	217	**µg/L**
Nitrosomorpholine	190	200	208	203	216	**µg/L**
Nitrosopyrrolidine	198	212	208	205	219	**µg/L**
Nitroso-N-Methylethylamine	192	197	193	199	219	**µg/L**
Nitrosodiethylamine	195	195	183	204	221	**µg/L**
Nitrosopiperidine	189	195	191	199	217	**µg/L**
Nitroso-N-propylamine	178	177	106	201	207	**µg/L**
Nitroso-N-butylamine	83	75	16	176	156	**µg/L**

Table 5. Results from stability studies with aldehydes at concentration 2 g/L and duration 48 days. Individual sample conditions are given in table.

Analyte	2 g/L Room temp. – light exposed 48 days	2 g/L Room temp. 48 days	2 g/L +4°C 48 days	2 g/L -20°C 48 days	Unit
Formaldehyde	1,87	1,99	1,96	2,34	**g/L**
Acetaldehyde	1,80	1,93	1,94	2,14	**g/L**

Table 6. Results from stability studies with aldehydes at concentration 200 µg/L and duration 21 days, stored in glass vials. Individual sample conditions are given in table.

Stored in glass vials						
Analyte	**200 µg/L Room temp. – light exposed 21 days**	**200 µg/L Room temp. 21 days**	**200 µg/L 50°C 21 days**	**200 µg/L +4°C 21 days**	**200 µg/L - 20°C 21 days**	**Unit**
Formaldehyde	<1	2	54	60	234	**mg/L**
Acetaldehyde	< 1	< 1	27	< 1	215	**mg/L**

Table 7. Results from stability studies with aldehydes at concentration 200 µg/L and duration 21 days, stored in HDPE vials. Individual sample conditions are given in table.

Stored in HDPE vials						
Analyte	**200 µg/L Room temp. – light exposed 21 days**	**200 µg/L Room temp. 21 days**	**200 µg/L 50°C 21 days**	**200 µg/L +4°C 21 days**	**200 µg/L - 20°C 21 days**	**Unit**
Formaldehyde	125	135	196	184	241	**mg/L**
Acetaldehyde	5	7	154	149	235	**mg/L**

Table 8. Results from stability studies with aldehydes at concentration 200 µg/L and duration 21 days, treated with DNPH, stored in glass vials. Individual sample conditions are given in table.

Stored in glass vials (treated with DNPH)						
Analyte	**200 µg/L Room temp. – light exposed 21 days**	**200 µg/L Room temp. 21 days**	**200 µg/L 50°C 21 days**	**200 µg/L +4°C 21 days**	**200 µg/L - 20°C 21 days**	**Unit**
Formaldehyde	302	274	348	244	30	**mg/L**
Acetaldehyde	597	461	597	417	34	**mg/L**

Table 9. Results from stability studies with amides at concentration 2 g/L and duration 61 days. Individual sample conditions are given in table.

Analyte	2 g/L Room temp. – light exposed 61 days	2 g/L Room temp. 61 days	2 g/L +4°C 61 days	2 g/L -20°C 61 days	Unit
Formamide	2,07	1,95	2,01	2,17	**g/L**
Acetamide	0,00	0,00	1,86	2,04	**g/L**

Table 10. Results from stability studies with amides at concentration 2 mg/L and duration 34 days, stored in glass vials. Individual sample conditions are given in table.

Stored in glass vials						
Analyte	**2 mg/L Room temp. – light exposed 34 days**	**2 mg/L Room temp. 34 days**	**2 mg/L 50°C 34 days**	**2 mg/L +4°C 34 days**	**2 mg/L -20°C 34 days**	**Unit**
Formamide	1,75	2,04	1,98	2,13	2,09	**mg/L**
Acetamide	0,39	1,97	3,13	3,11	3,12	**mg/L**

Table 11. Results from stability studies with amides at concentration 2 mg/L and duration 34 days, stored in HDPE vials. Individual sample conditions are given in table.

Stored in HDPE vials						
Analyte	**2 mg/L Room temp. – light exposed 34 days**	**2 mg/L Room temp. 34 days**	**2 mg/L 50°C 34 days**	**2 mg/L +4°C 34 days**	**2 mg/L -20°C 34 days**	**Unit**
Formamide	2,03	1,93	2,14	2,17	2,10	**mg/L**
Acetamide	2,30	1,85	3,13	3,18	3,17	**mg/L**

APPENDIX 5:

Cross validation of methods

Cross validation of the analysis methods was performed between SINTEF Materials and Chemistry, and the Norwegian Institute of Air Research (NILU). Analysis methods used at SINTEF are described in Appendix 2, and methods from NILU are described below. Nitrosamine concentrations in unknown cross validation samples 'A' through 'J' as measured by SINTEF and NILU are shown in Table 1.

Table 1. Concentrations of nitrosamines NDELA, NDMA and NPz in spiked samples as measured by SINTEF and NILU. Grey, spiked concentrations (from stock solutions); blue, concentrations measured by SINTEF; red. concentrations measured by NILU.

Sample ID	NDELA			NDMA			NPz			Unit
	Spike	SINTEF	NILU	Spike	SINTEF	NILU	Spike	SINTEF	NILU	
Sample A	0	4	< 30	0	< 2,5	**	0	<0,5	< 30	µg/L
Sample B	100	98	99	100	97	143	100	99	71	µg/L
Sample C	200	197	193	200	196	275	200	204	152	µg/L
Sample D	400	395	367	400	396	497	400	415	310	µg/L
Sample E	1000	967	952	1000	984	1294	1000	1044	724	µg/L
Sample F	500	502	473	500	494	640	500	520	367	µg/L
Sample G	500	483	503	500	483	662	500	523	352	µg/L
Sample H	500	481	543	500	486	670	500	523	368	µg/L
Sample I	500	482	505	500	486	623	500	526	359	µg/L
Sample J	500	463	435	500	478	684	500	525	330	µg/L

**Confirming ion not detected for this sample.

The method used at NILU Was as follows:
The nitrosamines (NDMA, NDELA, NPZ) were analyzed by high performance liquid chromatography combined with high resolution mass spectrometry (Time-Of-Flight). The analytical column was an Atlantis T3, 3 µm, 2.1x150 mm, using 10 mM ammonium acetate in water and methanol as the mobile phase at a flow rate of 0.2 mL/min. The first 4 minutes of the chromatogram was directed to waste using a divert valve. The extracted ion chromatograms had a typical mass peak width of 20 mDa. Target ions and confirming ions for the nitrosamines are shown in Table 2.

Table 2. Ionization mode, target ions and confirming ions used in analysis of nitrosamines at NILU.

Nitrosamine	Ionization mode	Target ion (m/z)	Confirming ion (m/z)
NDMA	ES +	75	ND*
NDELA	ES +	135	104
NPZ	ES +	116	86

*Not detected at the selected cone voltage. The sample A has a signal at m/z 75 which corresponds to the retention time of NDMA. Due to lack of confirming ion and a low signal-to-noise ratio the criteria are not fulfilled for a positive identification of the peak as NDMA.