Sampling and analytical procedures for potentially harmful components related to amine-based CO2-capture

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Author(s)/Source(s):	
Audun Gangstad, Bjarne Nenseter	
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Table of contents

1 Summary

The sampling and analytical procedures given in this document are the result of the technology qualification program in the CCM-project (2010-2013). The program included:

- Method development studies performed by 5 companies for the CCM project on synthetic samples (2010-2012)
- Practical use of the procedures on real/degraded samples from four verification plants. Some 1000 samples and 10000 analysis were performed (2012-2013) from various solvent systems

The procedures cover all parts of flue gas sampling and analysis as indicated in the Figure 1 and Table 1 below, in addition is preservation and analysis of wash water and solvent samples included.

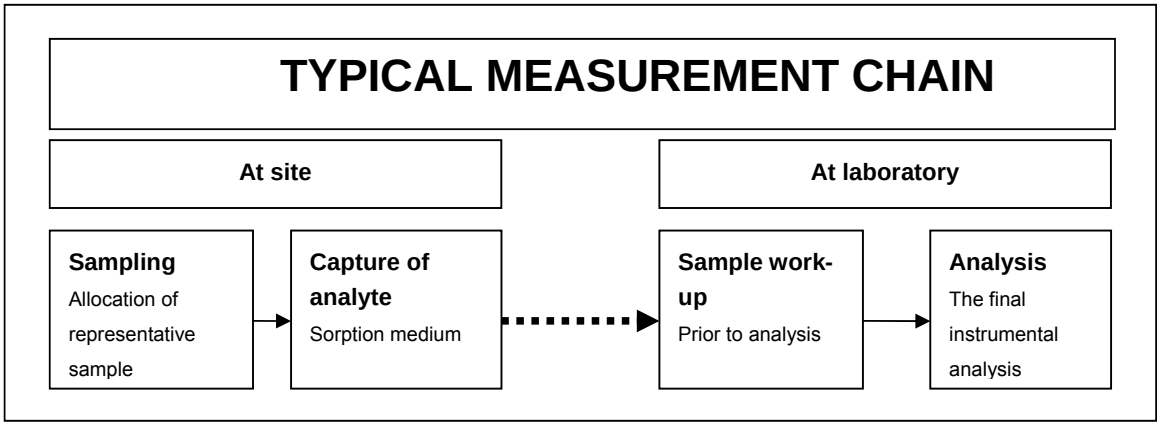

Figure 1.Typical measurement chain

Table 1.Main principle for the various steps

Sampling	**Flue gas:** The sampling must be done isokinetically in order to achieve representative samples with regard to droplets **Liquid samples** (wash water and solvent): Sampled from a representative circulating process volume
Capture of analyte from flue gas	Condensate bottle followed by liquid absorbents (sulfamic acid for nitros/nitramines and sulphuric acid for the rest)
Preservation and storage of samples	Sulfamic acid added to quench nitrite. Sulphuric acid pH adjustment. Samples to be frozen (-18°C) on site and shipped frozen, using cooling medium and insulated transport box.
Sample work up	Dependent on analyte; liquid-liquid extraction with DCM and ethylacetate (nitros/nitramines), derivatization with DNPH for aldehydes
Instrumental end detection	(HR)GC/MS (nitrosamines) IC (ammonia) Chemiluminescence detector (Total nitrosamines) LC/MS-MS (nitrosamines, nitramines, solvent amines, alkylamines) LC-UV (aldehydes)

2 Introduction

2.1 General/Background

There are no international standards that describe the sampling and analysis of amines and amine degradation products in flue gas. Hence, CCM has performed development work to establish such procedures. The work started in 2010 and the objective was to have well documented procedures for potential harmful components ready for use when the qualification of CO2-capture technologies started. Generic amines like MEA, AMP and PZ was used in this work, and the samples were syntetic. The former version of this document was produced based on this knowledge.

When the qualification program started (2012) CCM received real (degraded) samples from the various vendors, and also isokinetic samples were performed at the verification plants. Four solvent systems have been used in this work. Altogether some 1000 samples have been sampled and some 10000 analysis performed. The learnings from this comprehensive work is now included in this final version of this document.

2.2 Sample types

The sample types include:

- Water based condensate from flue gas sampling
- Absorbent solutions (0.1 M sulfamic acid, 0.05M sulphuric acid) for flue gas sampling
- DNPH-cartridges (for aldehylde sampling from flue gas)
- Wash water
- Solvent incl aminoacidsalt
- Reclaimer waste

2.3 Sampling principle

The sampling procedures include extraction of representative sample and capture of analyte, i.e. the work to be performed at site. The recommended sampling procedures should be:

- Scientifically representative; tested and verified for the specific amine degradation products / component groups / analytes.
- Possible to adapt and establish for practical performance at several different executors/locations. Hereunder a simplified sampling train setup, a minimum of equipment and chemical needs and optimization for subsequent laboratory analysis are important.

A good principle for flue gas sampling states that at least two barriers for analyte collection should be included in the method to secure an acceptable uncertainty. The rule for proper sampling (Leithe, W (1968), BUWAL (2001)):

> *"The last collection phase is used as a control for completeness of adsorption and may not contain more than 10 % of the total amount included. If in the last adsorption more than 10 % is recorded, the result must be questioned (greater uncertainty) or be discarded."*

2.4 Analysis/Compounds

The compounds of interest includes, but are not limited to, those given in Table 2 below

Table 2. Compounds of interest

Compound group	Compounds	CAS-nr
N-Nitrosamines, generic: "EPA 521 -mix" + NMOR	N-Nitrosodimethylamine (NDMA) N-Nitrosomethylethylamine (NMEA) N-Nitrosodiethylamine (NDEA) N-Nitrosodi-n-propylamine (NDPA) N-Nitrosodi-n-butylamine (NDBA) N-Nitrosopyrollidine (NPYR) N-Nitrosopiperidine (NPIP) N-Nitrosomorpholine (NMOR)	62-75-9 10595-95-6 55-18-5 621-64-7 924-16-3 930-55-2 100-75-4 59-89-2
N-Nitrosamines, solvent specific	Non-disclosure	Non-disclosure
N-Nitrosamines, total method (TONO)	Total amount nitrosamines	n/a
Nitramines, solvent specific	Non-disclosure	Non-disclosure
Nitramines, generic	Dimethylnitramine Diethylnitramine	4164-28-7 7119-92-8
Solvent amines	Non-disclosure	Non-disclosure
Alkylamines	Methylamine Ethylamine Dimethylamine Diethylamine Methylethylamine	74-89-5 75-04-7 124-40-3 109-89-7 107-15-3
Aldehydes	Formaldehyde Acetaldehyde	50-00-0 75-07-0
Ammonia	Ammonia	7664-41-7
Nitrite	Nitrite by "untreated TONO"	14797-65-0

3 Recommended sampling procedures

3.1 General/HSE

The procedures given here describe sampling of emission components from flue gas. It has been concluded that isokinetic sampling is required, since droplets most probably will exist in the emission and compounds of interest will be totally or partly solved in these droplets. Hence, a representative sample must be extracted with the same rate as the velocity in the sampling point.

It should also be mentioned that sampling from liquid systems (wash water and solvent) is considered conventional; samples are collected from circulating/mixed liquid process volumes, avoiding accumulation zones and dead volumes.

HSE-considerations are very important when performing sampling in environments like this. This must be coordinated with site owner when planning the work and local operations (e.g. control room, operational manager) when performing the work. CCM experience is that access to suitable laboratory facilities (e.g. fume hoods, lab bench space and general laboratory equipment) should be agreed upon during planning.

3.2 Proposed sampling-train setup

3.2.1 Main principle

The main recommended principle for capturing the relevant compounds/analytes is:

(1) to first have a condensation flask to collect as much of the humidity and analytes as possible, followed by
(2) suitable liquid absorbents which serves as backup to secure no breakthrough of analytes through the sampling train.

Characteristics of the flue gas in the CCM-case (gas fired power plant) that supports this setup is:
stack temperature in the region 30-50°C, water-soluble analytes and droplets will most probably exist

3.2.2 Two proposed configurations

Given the main principle stated above, two alternative configurations are proposed. Please see figures Figure 2 and Figure 3 below

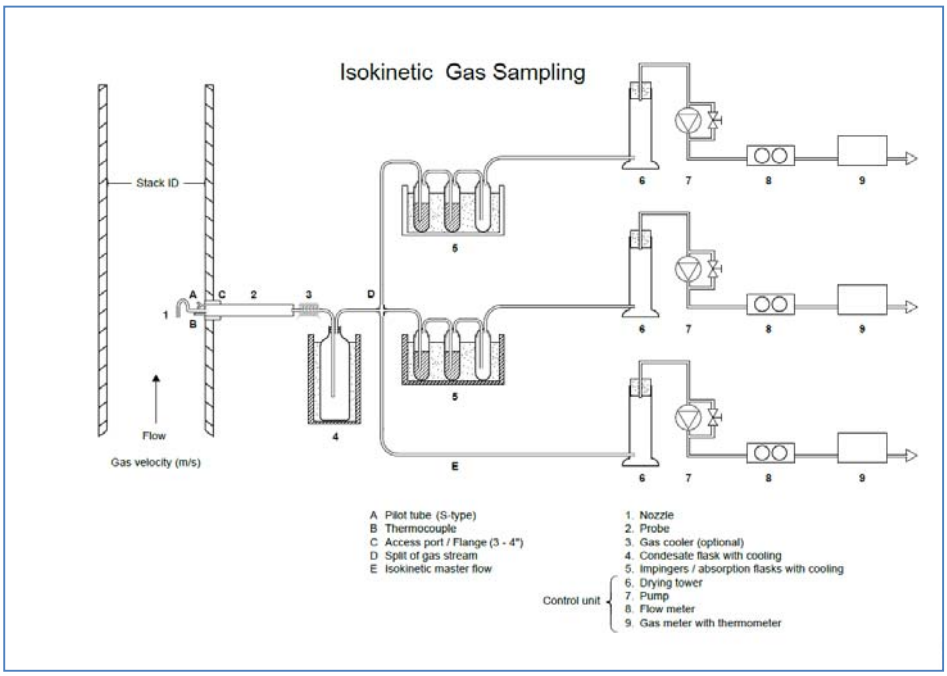

Figure 2 Sampling train setup with split downstream condensate flask (For "higher" gas velocities - Two side streams with absorbent flasks and one main stream for adjustment to isokinetic sampling rate)

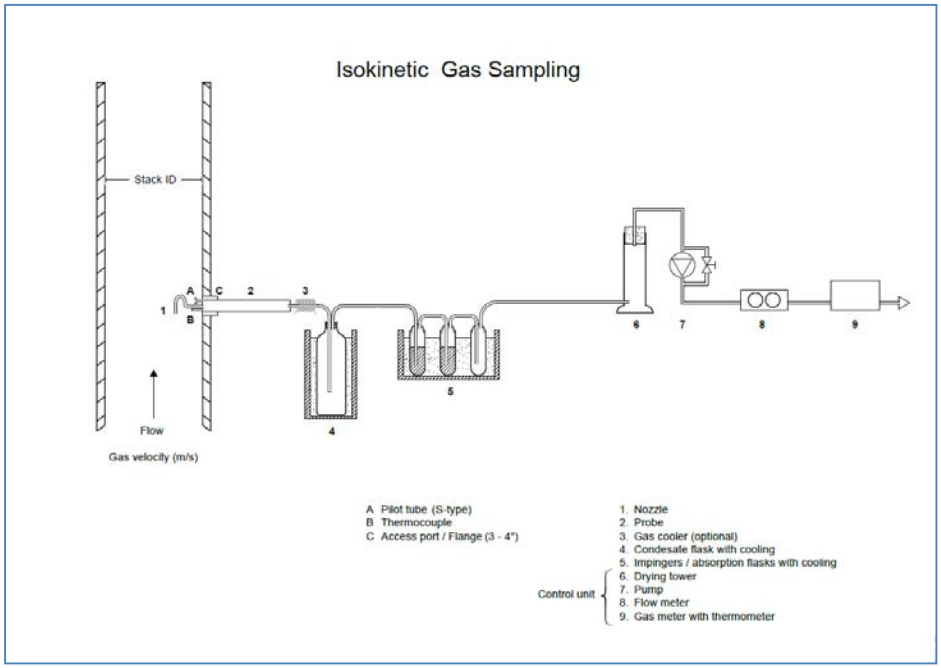

Figure 3 Sampling train setup - no split (For "lower" gas velocity – one main stream with absorbent flasks)

"No split" meaning sampling train with main stream only. "Split" meaning sampling train with side streams for capture of analytes and main stream for adjustment of isokinetic conditions.

It is essential that the condensation step is dimensioned with high condensation capacity, i.e. cooling capacity must be sufficient to lower the temperature in the sampled gas to well below flue gas dew point. This will secure that:

- This step will be the main capture step for relevant compounds (mostly very water-soluble)
- Chance of breakthrough of compounds through the whole train will be minimized
- Analytical laboratory will be able to perform analysis on a water-matrix where the main part of the analyte is found. This will lead to lower quantification limits compared to analysis in e.g. 0.1 M sulfamic acid
- Enable the choice for split downstream the condensate flask (to repeat: the gas must be dry in order for this to be scientifically amenable)

The second step (liquid absorption) is divided in separate absorbent flasks to be able to document the potential successive analyte concentration decline. CCM experience indicates that two absorbent flasks are sufficient, as most of the analytes are captured to a high degree in the condensate flask upstream these absorbent flasks. Also, an entrainment flask downstream these two absorbent flasks are recommended in order to verify that there is no carry-over in the sampling train.

Sampling of aldehydes is proposed to perform separately (but still iso-kinetically) due to use of solid phase cartridges with much lower flow capacity. CCM has performed simultaneous sampling of aldehydes with the liquid absorbents (i.e. three side streams and one main stream). It is doable, but not recommended when the gas flow in the side streams are not in the same range.

3.2.3 Main differences between the two configurations

Both configurations presented are recommended *as long as the isokinetic sampling rate can be obtained in a robust way*. This must be considered from case to case. However, the most important factor with regard to this is the isokinetic sampling rate (L/min) in the sampling train versus gas velocity in the stack.

Some advantages with the split solution:

- Easier applicable for "high" gas velocity
  - It can be challenging to dimension the sampling train without a split and still have isokinetic conditions.
  - The total sampling rate will in this case be divided into several sidestreams
  - Nozzle size can be within requirements in standard methods even at "higher" stack velocities (see chapter 3.3.1)
- Simultaneous sampling of analytes
  - removing the uncertainty due to variable process conditions
  - less time-consuming

The most important challenge with split solution is that the cooling capacity of the condensate step must be sufficient during the sampling periode. An advantage with "no split" is that the same gas volume is going through both the condensate flask and the absorbent flasks, and hence the limit of quantification should be the same in both solutions (given the somewhat unlikely assumption that matrix effects has no impact)

Please see chapter 0 for further discussion

3.3 Considerations - choosing sampling train configuration

When choosing a sampling train setup it is important to point out that many factors must be considered in order to configure a robust, practical and efficient sampling train. An overview of this is given in Table 3.

Table 3 Factors and considerations

Factors	Consideration	Influences
Stack (gas) velocity	Stack velocity is a very important factor, both when choosing split or no split but also for dimensioning the components in the sampling train. The temperature in the stack must be considered together with the velocity, since the flue gas is saturated with water. Hence, the volume of condensate pr timeunit will be affected by both these factors. According to EN 13284 the range for isokinetic sampling is 3-50 m/s. See chapter 3.3.1 for further information. At higher stack velocities (f.x. >15 m/s) it should be considered to use impingers in stead of absorbent flasks. Also, an additional barrier for collecting droplets leaving the flasks/impingers should be evaluated.	Nozzle size Split or no split Dimensioning of condensate bottle and absorbent flasks. Type of absorbent flask
Stack temperature/humidity	With water-saturated gas it is important to choose correct condensate bottle size. Cooling capacity must be evaluated (combined with ambient temperature)	Dimensioning of condensate bottle
Stack pressure	If there is negative pressure in the stack, care must be taken when sampling in order to avoid back-flush of liquids in the sampling train. In the case of significant overpressure and potential hazardous components in the flue gas – HSE/PPE must be evaluated	Operational procedure
Stack diameter	This affects how many sampling points are needed traversing the stack. This is covered in ISO-standards for isokinetic sampling. In addition, CFD-modelling can be used to give additional information about the flow conditions in the sampling plane.	Number of sampling points traversing the stack
Ambient temperature	Since the sampling principle is to condensate as much of the humitidy as possible in the condensate bottle, ambient temperature will influence on how much cooling medium will be needed. Obviously, the higher the ambient temperature – the more water ice/dry ice will be needed.	Amount of cooling medium for condensate bottles and absorbent flasks
Quantitification limit (LOQ) in analytical methods and target result (e.g. regulatory requirements)	Sampling time must be chosen so that sufficient material is collected in condensate bottle (and sufficient gas amount is bubbled through absorbent flasks) Ref chap 3.7	Sampling time, dimensioning of condensate bottle and absorption train
NOx level in flue gas	The higher the NOx level the more important it is to stabilize the samples after sampling is finished, see chap 3.7 and preservation routine Appendix A	Operational procedure

3.3.1 Determine nozzle size and isokinetic sampling rate

Optimal isokinetic sampling rate using regular components (incl absorption flasks and pumps) in the sampling train is in the range of 3-12 L/min. This is based on experience. ISO 11338-1 states that sampling rate should be lower than 15 L/min. EN 13284-1 states that "…it is recommended to use nozzles of inside diameter exceeding 8 mm, and diameters less than 6 mm shall be avoided."

Based on this, Table 4 below could be used to establish what isokinetic sampling rate and nozzle size to use:

1. Stack velocity is given
2. For that given stack velocity find a isokinetic sampling rate where the nozzle size is larger than 6 mm preferably (it can be necessary at higher stack velocities to compromise on this requirement and lower the acceptable nozzle size to 4 mm).
3. In this way both the nozzle size and the isokinetic samling rate which the pump(s) must be adjusted to is given.
4. At higher stack velocities (f.x. higher than 15 m/s) it should be considered to use the "split" setup (given in Figure 2 above). in order to lower flow rate in the side streams (absorbent flasks), and hence minimize risk for carry over of liquids and breakthrough of analytes in the sampling train. At these higher stack velocities it is very important to secure sufficient cooling capacity for the condensate bottle upstream the split point.
5. At lower stack velocities both alternatives can be used. If split solution is preferable the nozzle size can be increased accordingly to maintain isokinetic conditions.

Table 4 Nozzle size (mm) vs stack velocity and sampling rate

	Isokinetic sampling rate (L/min)							
Stack velocity (m/s)	2	4	6	8	10	12	16	20
2	4,6	6,5	8,0	9,2	10,3	11,3	13,0	14,6
4	3,3	4,6	5,6	6,5	7,3	8,0	9,2	10,3
6	2,7	3,8	4,6	5,3	5,9	6,5	7,5	8,4
8	2,3	3,3	4,0	4,6	5,2	5,6	6,5	7,3
10	2,1	2,9	3,6	4,1	4,6	5,0	5,8	6,5
12	1,9	2,7	3,3	3,8	4,2	4,6	5,3	5,9
14	1,7	2,5	3,0	3,5	3,9	4,3	4,9	5,5
16	1,6	2,3	2,8	3,3	3,6	4,0	4,6	5,2
18	1,5	2,2	2,7	3,1	3,4	3,8	4,3	4,9
20	1,5	2,1	2,5	2,9	3,3	3,6	4,1	4,6

Ref: Analysis and sampling methods, Rambøll (2012). http://www.gassnova.no/gassnova2/frontend/files/CONTENT/Rapporter/Analysisandsamplingmethods_Ramboll.pdf

3.4 Main equipment for recommended sampling train set-up:

Below is listed main equipment for the sampling train, with recommended material and other characteristics.

Nozzle:
Stainless steel, titanium or glass, size: typical range 4 – 10 mm, absolute lower recommended inner diameter: 3,5 mm

Probe:
Standard type. Material: stainless steel, titanium or glass. Optional: with cooling possibility

Condenser:
Condensate flask with suitable cooling unit (cooling bath (ice, dry ice/water). Circulation compressor cooler) capable for temperature reduction of the extracted gas sufficiently below the dew point of the stack gas. A temperature at the condenser

outlet below 10°C is recommended. Optional: additional gas cooler (e.g. glass coil) between probe and condensate flask. It's important that the actual conditions like flue gas and ambient temperature are considered when dimensioning the cooling system and capacity for the probe, additional cooler and condenser.

Liquid absorption unit:
Three gas washing bottles (250 – 500 mL glass bottles with frit) suited for isokinetic gas sampling (typical: 3 – 12 L/min sampling rate), two filled with absorption solution and one empty bottle for catching carry over/droplets.
Empty condensate flask (any liquid trapped should be analysed as a sample, volume must be noted, no preservation needed).
Cooling bath: for liquid absorption bottles, filled with cooling media (ice, dry ice and water), cooling temperature 1 – 5°C.

Control and suction device units:
Gas dryer, gas pump, flow meter, gas meter, dimensioned for the sampling site and purpose.

In addition:
The following measurement device units can include: Pitot tube (S-type), micromanometer, thermometer, control unit for isokinetical sampling, data storage unit, tubing and connections.

3.5 Sorbent mediums for the various analytes

Table 5 Overview over sorbent mediums and preservation for the various analytes

Compound group	Capture of analyte
Specific non-alcoholbased nitrosamines	Condensate + 0,1 M (9,7 g/L) sulfamic acid
Specific alcoholbased nitrosamines	"
Total nitrosamines	"
Nitramines	"
Solvent amines	Condensate + 0,05 M sulphuric acid
Alkylamines	Condensate + 0,05 M sulphuric acid
Aldehydes	Condensate + DNPH-cartridge (e.g. Sep-Pak DNPH-Silica Plus Long Cartridge, 800 mg, Waters) Alt: Condensate + DNPH (EPA 0011, EPA 8315A)
Ammonia	Condensate + 0,05 M sulphuric acid Alt: Condensate + boric acid (JIS K 0099:2004)

3.6 Relevant international standards

Emission sampling of typical components from amine based CO2 capture plants are not covered by a suitable international standard. However there are several relevant standards describing requirements for design/sampling sites and for general isokinetic sampling performance. Some of the most important are:

- EN 15259:2007, Air quality. Measurement of stationary source emissions. Requirements for measurement sections and sites and for the measurement objective, plan and report
- EN 13284-1:2002, Stationary source emissions. Determination of low range mass concentration of dust – manual gravimetric method

- EN 14385:2004 Stationary source emissions. Determination of the total emission of As, Cd, Co, Cu, Mn, Ni, Pb, Sb, Ti and V.
- EN 1948-1:2004, Emissions from stationary sources – Determination of the mass concentrations of PCDD/PCDF and dioxin like PCBs – Part 1: Sampling
- US EPA method 1 A: (10-30 cm duct)
- ISO 11338-1:2003, Stationary source emissions – Determination of gas and particle-phase polycyclic aromatic hydrocarbons – Part 1: Sampling
- ISO 3936, Annex A: 2008, Measurement of fluid flows in closed conduits – Velocity area method using Pitot Tubes
- EPA 0011 and EPA 8315A, Aldehyde sampling and analysis

3.7 Operational sampling procedure

Isokinetic sampling should be performed according to relevant international standard method, e.g. EN 15259 and EN 13284-1. The detailed operational procedure must be based on local conditions at site and equipment available and is therefore not given here.

However, in the case of sampling from amine CO2-capture plants, the following should be taken into consideration:

1. **Sampling time:**
   The duration of sampling need to be determined based on LOQ of the actual analytical procedures, process conditons and practicalities at site. In practice sampling time of 2-3 hours often is applicable. It is recommended (especially during first time sampling) to use two different sampling times in order to establish potential errors in sampling procedure and to optimize sampling time.
2. **Cooling of condensate flask and absorbent flasks:**
   Sufficient amount of cooling medium (e.g. water/ice/dry-ice) to secure necessary cooling of condensate bottle and absorbent flasks are essential. In hot ambient conditions additional cooling of probe and a separate gas cooler should be considered. Temperature in cooling bath should not exceed $5^{o}C$
3. **Preservation of samples:**
   In order to make sure that no nitrosation take place during storage of samples, a specific preservation routine was developed by the CCM-project. See Appendix A. This procedure is particularly important when NOx-concentration in the flue gas is high (e.g. above 10 ppm) and the solvent has a high nitrosation potential. The procedure should be carried out directly after sampling (before freezing on site/shipment to analytical laboratory).
4. **Storage and shipment:**
   Sample material from condensate flask and absorbent flasks should be transferred to separate plastic bottles (e.g. polypropylene or highdensity polyethylene). Keep protected from light. All samples should be frozen (approx. -18°C) on site the same day as sampled.
   CCM has performed investigations with regard to stability of real/degraded samples - and shown that the analytes given in Table 2 were stable for at least 6 months (-18°C storage)

Main principle during shipment is to keep the temperature as close as possible to the pre-shipment storage temperature. Samples should be kept below 0°C during the whole shipment do avoid melting of the waterbased samples. Commercially available icepacks (waterbased, potentially with additives) are recommended as cooling medium. If the courier company propose other solution, that solution should be equally good for long term cooling effect inside the shipping box.

For the solvent samples it must be considered from case to case under what conditions they should be stored.

4 Recommended analytical procedures

Table 6: Overview over analytical procedures

Compound group	Sample workup	Instrument	Reference to international standards	Detection limit*, (µg/Nm3)
Specific non-alcoholbased nitrosamines	Liquid-liquid extraction w/DCM	GC-HRMS or GC/MS	EPA 521	0,005
Specific alcoholbased nitrosamines	Continuous liquid-liquid extraction w/ethyl acetate	LC/MS/MS (APCI)	-	1
Total nitrosamines	Heated chamber (80°C) containing a triiodide solution in acetic acid	Chemiluminescence detector	-	0,03 nmol (0,1µM**)
Nitramines	Liquid-liquid extraction w/ethyl acetate	LC/MS/MS	-	0,05
Solvent amines	None/dilution	LC-MS/MS	-	1-50
Alkylamines	None/Direct injection	LC-MS/MS	-	5
Aldehydes	DNPH-derivatization (for untreated samples)	LC-MS/MS or HPLC-UV	EPA 8315A	0,05
Ammonia	None	IC	JIS K 0099:2004	5000

* *based on sample volume = 0,5 m^3*

** *based on 300 µL sample volume used*

The analytical procedures are given in Appendix B

5 Future work

Preservation of samples:
In specially challenging cases (high NOx, high ambient temp, solvent with high nitrosation potential), pre-preservation of the condensate flask with concentrated solution of sulfamic acid should be considered. This was not performed by CCM in any sampling campaign during technology qualification phase. However, reaction kinetics has been investigated in laboratory by CCM-project, and it was concluded that this did not cause any significant nitrosation (even using very conservative values for the parameters mentioned above).

Aerosols/Mist:
This has not been investigated during CCM campaigns since it did not appear in the flue gas from gas burners. This can potentially be a challenge when sampling from coal-fired plants, and should be investigated in detail prior to sampling at such sites. One important issue can be breakthrough of analytes in the sampling train (mist mobility), mitigating actions could be high cooling capacity and special impingers in order to aggregate the mist.

Possible additional sampling features:
Optionally additional steps like filtration and solid adsorption may be included in the sampling. Filtration downstream condensation to remove mist/droplets is possible but so far not tested and verified for this purpose. Adsorption on solid resin (e.g. XAD, silica, activated carbon) post liquid absorption can be included as a back-up barrier. However these steps also increase the complexity in sampling equipment setup and the pressure drop. It will also demand additional analysis work.
Based on CCM experience these sampling features are not required.

Concentration of absorbent solution:
0.1 M (9.7g/L) of sulfamic has been used in this project as the absorbent solution when capturing nitrosamines. It should be investigated if 0.02 M would be sufficient to achieve a reasonable capture of nitrosamines. This would potentially improve the sample work-up and instrumental detection methods in the laboratory – and hence improve accuracy and quantification limits.

Aldehydes, EPA0011 vs DNPH-cartridges:
It should be validated with real/degraded solvent systems how the EPA0011 (using liquid DNPH-solution) performs compared to commercially available DNPH-cartridges. CCM experience (one solvent system) is that DNPH-cartridges give results in the same region as EPA0011. DNPH-cartridges are much easier use in practical work at site.

6 Calculation of results for flue gas samples

Results for flue gas condensate and absorbent solutions (in mass/L) are calculated from peak areas from external standard calibration curve

Quantity of analyte:

$$Q_{analyte} = C \times V_s$$

$Q_{analyte}$	quantity of analyte collected, in µg
C	is the concentration of the solution in mg/L (µg/mL)
V_s	is the volume of absorption solution in mL

Sampled gas volume:

For dry gas meter:

$$V_{std} = V_{T,\ p} \times \frac{273}{T} \times \frac{p - p_{res}}{101{,}3}$$

For wet gas meter:

$$V_{std} = V_{T,\ p} \times \frac{273}{T} \times \frac{p - p_s(H_2O)}{101{,}3}$$

V_{std}	the volume under standard conditions (0°C, 101,3 kPa) and dry basis, in cubic meters (m³)
V_{Tp}	the volume under actual conditions of temperature and pressure, on dry basis with "dry" gas meter or wet basis with "wet" gas meter, in cubic meters (m³);
T	Actual temperature in Kelvin
p	Total pressure in kPa at the gas meter
$p_s(H_2O)$	saturated vapour pressure at the temperature of the gas meter, in kilopascals (kPa);
P_{res}	is the residual vapour pressure, in kilopascals (kPa).

Final concentration in the flue gas is expressed as:

$$\mathbf{C_{analyte}\ [\mu g/m^3 n]} = \frac{Q_{analyte}}{V_{std}}$$

Appendix A. Preservation routine

Objective

Stabilize nitrite and amine containing samples in order to avoid post sampling nitrosation.

Principle

Equimolar, times a factor, amounts of sulfamic acid compared to nitrite is added to the samples to quench nitrite.

Chemicals

1. Sulfamic acid, p.a. quality.
2. Sulphuric acid, p.a. quality. Strength: Commercially available volumetric solutions from 1 M to concentrated (see #5 in Operational procedure below)
3. Deionized water (UHQ), 18.2 Mohm.

Reagents to be prepared by sampling company at site

1. Sulfamic acid, 10 g/L=0.1M (to be prepared separately for each campaign)

Equipment

1. Laboratory glassware
2. pH test strips
3. Pipette, manual or electronic. Range 100-1000 µL
4. Pipette, manual or electronic. Range 10 - 100 µL
5. Pipette tips suitable for the specific pipettes
6. Balance, 0.01 g accuracy
7. Nitrite analytical equipment (ion chromatography - IC)
8. Nitrite test strips
9. Freezer, -18°C

Operational procedure

1. Measure pH in sample using pH test strip.
    a. If pH is higher than 10, no preservation needed (no significant nitrosation takes place)
    Note: Solvent samples shall not be preserved, even if pH is lower than 10.
    b. if pH is lower than 10 continue with procedure as described below

2. Measure nitrite content in sample or use qualified estimate for the concentration.
    a. Preferrable analytical method for nitrite is based on ion chromatography (IC), e.g. ISO 10304-1:2007
    b. Possibly (for some matrixes – must be tested by sampling company) nitrite test strips also could be used

3. Prepare sulfamic acid solution
    a. Add 1 g of sulfamic acid to a 100 mL volumetric flask
    b. Add some UHQ-water and shake until dissolved
    c. Add UHQ-water to mark

    NOTE: This is the same concentration as 0.1M solution used in the sampling train, and hence the absorbent solution also can be used

4. Based on nitrite result - use appropriate pipette and add sulfamic acid to sample using corresponding value from the following tables. Shake a few times to homogenize the samples.

Table 7. Addition of sulfamic acid - 10 g/L sulfamic acid (~0.1 M)

		Sample size, mL			
		5	10	25	50
Nitrite, mg/kg	0,5	12,5 µL	25 µL	62,5 µL	125 µL
	1	25 µL	50 µL	125 µL	250 µL
	5	125 µL	250 µL	625 µL	1250 µL
	10	250 µL	500 µL	1250 µL	2500 µL

If result of nitrite strips is below detection limit then sulfamic acid amount should be added as if the nitrite result was equal to the detection limit. If, for instance, the detection limit is 0.5 mg/kg for the nitrite strips test and there is no color change on the strips when testing, a 10 mL sample should anyway be added 25 µL sulfamic acid (as given in Table 4)

In addition, in case of uncertain readings between two values, always take the conservative approach and choose the higher nitrite result.

5. Add sulphuric acid to pH < 2.
   The strength of the sulphuric acid should be so that the sample is not diluted more than 5% - hence it should be tested prior to sampling what specific strength to use.
   Use pH-strips to verify that pH is below 2.

   The pH must be lowered quickly when preserving samples. First establish necessary volume by titrating a practice sample (with the added sulfamic acid from Table 4) to pH <2. In the real samples to be preserved, this volume of sulphuric acid must be added in one operation.
   NOTE: End pH in the range 3 to 4 must be avoided, since this is the pH-range where the nitrosation potential is highest.

6. Sample storage until transport:
   All samples should be frozen (approx. -18°C) on site the same day as sampled. At the end of the campaign the frozen samples are ready for packing and shipment to analytical laboratory.

Appendix B. Analytical procedures

NOTE: *The procedures given below are based on generic amine (mainly MEA). Testsamples were syntetic and non-degraded. Adjustments have been made during solvent specific validation work at CCM Chemical analysis contractor (Rambøll, Finland) Q2-12 to Q2-13. Hence, the procedures do not reflect the excact analytical methods used when analyzing the real samples.*

Specific non-alcohol based nitrosamines

1. Principle

Samples, spiked with mass-labeled internal standards, are extracted with dichloromethane prior to analysis with GC-MS. (GC-HRMS where available)

2. Interferences

High concentration of solvent amines may interfere with the pretreatment and/or chromatographic separation. Maximum recommended solvent amine concentration is 5-10 %. If samples i.e. solvent samples) contain higher amounts of amine, they must be diluted accordingly before extraction)Reagents and standards

Reagents:

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

Standards:

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

Internal Standards:

N-Nitrosodimethyl-D6-amine (C/D/N Isotopes Inc.), Purity 98 %, Deuteration degree 98 %
N-Nitrosomorpholine-D8 (C/D/N Isotopes Inc.), Purity 98 %, Deuteration degree 98 %
1,4-Dinitrosopiperazine-D8 (Chiron AS), Purity 95%, Deuteration degree 98,6 %
N-Nitrosopiperidine-D10 (Chiron AS), Purity 99,8%, Deuteration degree 99,2 %
N-Nitrosodiethylamine-D10 (Chiron AS), Purity 99%, Deuteration degree 99,4 %

A stock solution should be made out to 10 mg/L concentration in methanol. External standards are diluted to the range of 10-500 µg/L.

3. Equipment

Standard laboratory equipment & glassware
GC with mass spectrometry detection, preferably high resolution MS.
TurboVap –automated evaporating apparatus or suchlike

4. Sample storage in laboratory

The samples should be analyzed as soon as possible after arrival to the laboratory.

Samples can be stored at +4°C for up to 2 weeks from time of sampling. If stored for longer periods than this, samples should be stored at -18°C

5. Procedure

Blank sample will be treated and analyzed exactly as the actual samples. Standard addition to the sample matrix will be done with each sample set. Recoveries will be monitored.

If the entire sample is planned to be analyzed the container must be weighed before and after extraction. Internal standards are added (10 µL of 10 mg/L) to the sample. When possible a spiked sample is done to the sample matrix. Otherwise spiked sample will be done to UHQ-water with similar solvent amine concentration and pH as in actual samples (synthetic matrix).

Samples (including standards and quality controls) are extracted twice with dichloromethane using total of 50mL solvent. If necessary e.g. at high solvent amine concentrations, the combined extracts are washed-up with 50 mL of 1M HCl- solution. The cleaned extracts are then dried with anhydrous NaSO4 and evaporated by TurboVap to 0.5 mL. Finally the samples are transferred to GC vials and analyzed. Analysis of samples is done with GC-MS system, GC-HRMS where available.

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

- Column: Restek Rtx-Dioxin2 (40m, 0.25 mm, i.d. 0,18 µm film)
- Carrier Gas: helium at constant flow of 1.2 mL/min.
- Injection: splitless injection 200°C, injection volume 1 µL.
- Oven program: 30 °C hold 5min, 10 °C/min to 120 °C, 5 °C/min to 140 °C, 10 °C/min to 220 °C and 30 °C/min to 320 °C hold 5 min (postrun).

Recommended resolution of mass spectrometry is at least 5000 (5% peak height). The monitored masses are:

Compound	m/z of analytes	m/z of perfluorokerosene reference peaks (lock mass)
N-Nitrosodimethylamine (NDMA)	74.0480	92.9952 or 99.9936
N-Nitrosodimethylamine-D_6	80.0851	
N-Nitrosodiethylamine (NDEA)	102.0793	99.9936
N-Nitrosodiethylamine-D_{10}	112.1411	
N-Nitrosomorpholine (NMOR)	86.0606 (and/or 116.0586)	92.9952 or 99.9936
N-Nitrosomorpholine-D_8	94.1100 (and/or 124.1080)	
N-Nitrosopiperidine (NPIP)	114.0793	99.9936
N-Nitrosopiperidine-D_{10}	124.1411	
1,4-Dinitrosopiperazine (DNPIPA)	84.0687 (and/or 114.0668)	92.9952 or 99.9936
1,4-Dinitrosopiperazine-D_8	92.1182 (and/or 122,1162)	

Specific alcohol-based nitrosamines

1. Principle

Samples –spiked with mass-labeled internal standards- are extracted with ethyl acetate using a specific Continuous liquid-liquid extraction setup. The extract is subsequently analyzed using LC/MS-MS.

2. Scope and Limitations

This procedure covers the analysis of NDELA in wash water samples.
It should be applicable for other nitrosamines which have poor recovery using the DCM-extraction given in “Specific non-alcoholbased nitrosamines”-procedure in this document, but this must be tested prior to use.
It should also be applicable for other sample types like solvent (diluted) and condensate/sorbent solutions from emission sampling, again – this must be tested prior to use.

3. Sample storage in laboratory

The samples should be analyzed as soon as possible after arrival to the laboratory. Samples can be stored at +4°C for up to 2 weeks from time of sampling. If stored for longer periods than this, samples should be stored at -18°C.

4. Extraction and Concentration Procedure

1) Take 500 mL of quenched wash water (with 2.0 g/L of sulfamic acid at pH 2) and dilute it to 1 L with deionized water
2) Measure the pH of the 1 L sample and raise the pH up to pH 5.5-6 with NaOH
3) Spike the 1 L sample with 20 □g/L deuterated d_8-N-nitrosodiethanolamine (10 □L of a 2.0 g/L NO-DELA-d_8 stock in acetonitrile)
4) Extract 1 L sample with 400 mL ethyl acetate using a continuous liquid-liquid extractor (CLLE) for 24 h
5) Remove ethyl acetate from extractor and rotovap at 37°C under vacuum to ~ 10 mL.
6) Blow remaining ethyl acetate extract down to dryness over a 1 mL bed of deionized (DI) water allowing for mass transfer into the aqueous phase
7) Inject the 1 mL water sample on the LC/MS/MS

5. Instrumental analysis

These compounds were analyzed on an LC/MS/MS (Varian 500-Ion Trap MS) with atmospheric pressure chemical ionization (APCI) in positive mode. The specific chromatographic parameters used are listed below:

- LC Column: Agilent Hi-Plex ligand exchange column (300 x 6.5 mm, 8 μM)
- LC Flow Rate: 0.3 mL/min
- LC Eluent: 100% of 30 mM formic acid in water
- Injection Volume: 50 μL

The drying gas (N_2) and vaporizing gas (N_2) temperatures for the APCI unit were set to 250°C. Additional compound-specific parameters for the MS/MS were optimized and are listed in the table below. The final instrument detection limits were 200 nM NDELA.

Compound	Parent Ion (M+1)	MS-MS Daughter Ions	Capillary Voltage (volts)	RF tuning (%)	Excitation Amplitude (volts)
NDELA	135	74+86+104	30	53	0.7
NDELA-d_8	143	80+111	30	53	0.2

Total nitrosamine content

1. Principle

The specifics of the total nitrosamine assay are provided in Kulshrestha et al. (2010). Briefly, a sample is injected into a chamber heated at 80 °C containing a triiodide solution in glacial acetic acid (Figure 3.21). This acidic solution reduces nitrosamines to nitric oxide (NO^*) which is purged from the vessel under a nitrogen gas stream. After passing through a cold temperature condenser and a base trap, the gas enters a chemiluminescence detector. In the detector, ozone oxidizes NO^* to excited state nitrogen dioxide (NO_2^*). Relaxation of the nitrogen dioxide emits a characteristic photon that is detected by a photometer.

2. Interference and limitations

In addition to N-nitrosamines, only nitrite and S-nitrosothiols have been found to emit NO^* by this reaction chamber. Accordingly, it is important to pre-treat samples to quench nitrite.

3. Reagents and standards

Intentionally left blank, see section 6 below

4. Equipment

Standard laboratory equipment & glassware
Ecophysics CLD 88sp chemiluminescence detector

5. Sample storage in laboratory

The samples should be analyzed as soon as possible after arrival to the laboratory. Samples can be stored at +4°C for up to 2 weeks from time of sampling. If stored for longer periods, samples should be stored at -18°C

6. Procedure

Photograph of the total nitrosamine reaction chamber:

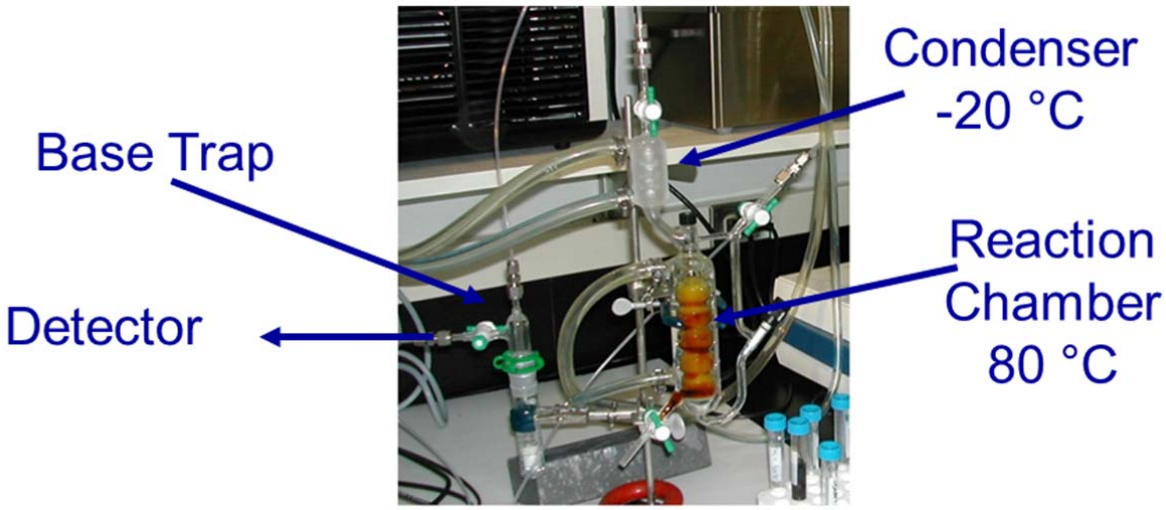

Figure 4. Photograph of TONO laboratory setup

1) System warm-up

Turn on 80 °C bath for reactor jacket. Check water level.

Turn on -20 °C bath for condenser - flip switch upwards. Refill with antifreeze only.

Turn on CLD 88sp – switch on the back. Readings will show up on front screen after about 30 min. Range should be 1000.

2) Base Trap

Base trap liquid is good for a few days. Change liquid if the system is not used for more than three days.

Fill with 100 mL 1 N NaOH

Use high vacuum grease and clamp to prevent leak and reduce etching of glass

Cool base trap with ice-water mixture. Make sure there is solid ice throughout the run, as increasing temperature will lead to unstable background

3) Reaction chamber

Prepare I_3^- solution: Make stock fresh daily. Weigh 2.7 g potassium iodide and 0.57 g iodine; dissolve in 5 mL deionized water.

Clean reaction chamber: Turn on N_2 gas and rinse reaction chamber with DI, MeOH, DI, and then glacial acetic acid. Make sure there is gas flow when there is liquid in the chamber.

Fill reaction chamber: Add 15 mL glacial acetic acid to the reactor. Adjust gas flow so that liquid surface is below the neck of the reactor. Add 1 mL of I_3^- solution from clean plastic syringe.

Add condenser: Make sure no tube is connecting to the base trap. Apply a little vacuum grease and tighten clamp to prevent leak. Adjust gas flow so that liquid surface is below the neck of the reactor (my need readjustment due to the increased resistence)

Connect the tube to the base trap. Reading on pressure gauge downstream to base trap should not exceed 1 psi.
Normally reading is slightly negative (between -1 to 0 psi).

4) Samples

Prepare 5 mL 20 g/L mercuric chloride solution in deionized water. Stored in fridge. Good for two weeks.

Prepare 5 mL 50 g/L sulfanilamide solution in 1 N hydrochloric acid. Stored in fridge. Good for two weeks.

Add 100 μL mercuric chloride solution to 1 mL sample (organic solvent extract or aqueous sample), and store in dark for 30 min. Then add 100 μL sulfanilamide solution, and store in dark for 15 min.

Standard curve:

Treat 10 μM NDMA solution the same way as samples.

Inject 3, 5, 8, 10, 15, 20, 30 μL treated NDMA solution into the reaction chamber – corresponding to injected mass of 0.03, 0.05, 0.08, 0.10, 0.15, 0.20, 0.30 nanomole of nitrosamine.

5) Data collection

Wait until the reading on instrument front declines to ambient NO values (the reading on the screen when the system is not connected) or lower. Zero point may not be calibrated, but it does not affect data output. Usually there is an initial spike after the system is connected. If the reading doesn't go down within 10 min, may need to change tubing

Open Spiroware Desktop and then WBreath

Under sampling menu, set Duration to 3600 sec, Channels to NO only with frequency of 5

Under view menu, set channels to NO only with range of -10 to 5 ppb. This range can be changed during a run and it does not affect the final output.

Press the play button. Allow a minute to pass to see a stable baseline

In each run, inject samples in this sequence: check standard (similar mass with the measured sample), pretreated sample (both of the duplicates), another check standard, pretreated sample again, third check standard. Keep the list of samples in an excel spreadsheet.

After a run finishes, press stop button. Under File menu, save as MUSERN and then a number, and then export ASCII data – only export the NO values

6) Data analysis software

Open Chromprocessor – under programs.
Import files:
Import from Matrix directory the file exported from WBreath and follow prompts doing the least possible

Smoothing:
Set filter frequencies to 0% V1 and 7% V2, then press green check mark
Baseline correction:
Edit nodes using red squares to drag baseline to peak edges, then press green check
Under Analysis menu
Select peak picking – auto
Integration – manual: Drag red bars to surround peaks and read off areas

7) Shutdown

Disconnect reaction chamber to base trap, i.e. intake ambient air
CLD 88sp: press SYS button, and then Yes on front of instrument. Wait for flashing signal on the front screen to switch off.
Turn off both water baths.

Empty reaction chamber with gas still on, rinse with DI, MeOH and then DI.
Turn off N_2 gas.

Nitramines

1. Principle

Liquid-liquid extraction of samples using ethyl acetate is followed by LC/MS-MS detection. For piperazine-nitramine direct injection to LC/MS-MS is used. Until labeled standards are available, unlabeled standards are used for calculating extraction coeffisients

2. Equipment and chemicals

Equipment:
Glassware:

- extraction tubes with cap
- separation funnel
- reagent tubes for evaporation
- brown GC/LC autosampler
- vials w/ crimp on caps

Vortex tube mixer
Chemicals:
Ethyl acetate (<99%)
Potassium dihydrogen phosphate (p.a.)
Disodium hydrogen phosphate (p.a.)
Deionized water

3. Sample storage in laboratory

The samples should be analyzed as soon as possible after arrival to the laboratory.

Samples can be stored at +4°C for up to 2 weeks from time of sampling. If stored for longer periods than this, samples should be stored at -18°C

4. Liquid–Liquid Extraction (LLE)

Preparation of phosphate buffer solution: 15 g KH_2PO_4 and 50 g of Na_2HPO_4 is added to 100 mL of deionized water.
The pH of the buffer should be 7.4.

1) To the sample (2.5 mL condensate or wash water or 250 µL amine solvent) is added internal standard (50 to 100 ng/mL **NB: Deuterated internal standards are not available for the nitramines, per 2012-02-13)**
2) 3 mL of saturated phosphate buffer is added, and it is controlled that the pH is within 7 to 8 after mixing
3) 4.5 mL of ethyl acetate extraction solvent is added

4) The sample is extracted twice (2 x 4.5 mL) by vortexing
5) The ethyl acetate phases are combined and transferred to a new tube
6) The ethyl acetate phase (9 mL) is evaporated to a volume of ca. 1 mL with air
7) 200 µL of water is added to the ethyl acetate phase
8) This two phase solution is further evaporated until the ethylacetate phase is evaporated
9) The ca. 200 µL concentrated sample (mainly consisting of water) is transferred to an autosampler vial and capped.

5. Instrumental analysis

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

Analytical column:
Discovery HS-F5, (15cm x 2.1 mm, 3 µm), Supelco Analytical, St. Louis, MO, USA (CAT.NO: 567503-U)

Chemicals:
Ammonium acetate, AmAc (12 mM), HPLC quality
Acetonitrile, HPLC quality

Calibration:
Calibration is performed with calibration standards prepared in deionized water. The calibration standards are injected in one analytical series together with the unknown samples (diluted or prepared by LLE method). The calibration samples and the unknown samples must be added the deuterated internal standard before sample preparation and analysis. If unknown samples are diluted, the internal standard is added after dilution. If the unknown samples are to be prepared by LLE or SPE techniques, the internal standard is added before sample preparation. If the sample is to be concentrated by a high factor, the amount of internal standard added should be lowered by a corresponding factor. This will give a similar concentration of internal standard in all samples during the final instrumental analysis.

The following calibration ranges are suggested:

Analyte	*Calibration range*
MEA-nitramine	2.5-10000 µg/L
AMP-nitramine	10-10000 µg/L
Piperazine-nitramine	1-10000 µg/L

Five levels of concentration should be applied to generate a proper calibration function. If the concentrations in the unknown sample are higher than highest calibration standard, the sample should be diluted to a final concentration within the range given above prior to analysis. Calibration samples should always be analyzed together with the unknown samples in the same analytical series.

Chromatographic conditions:

Parameter	**Type/condition**
Column	Discovery HS-F5, (15 cm x 2.1 mm, 3µm)
Mobile phase	12 mM AmAc/ACN – 50/50
Flow	0.2 mL/min
Injection volume	5 µL

Retention times (LC-MS/MS):

Compound	**Retention time (min)**
MEA-nitramine	1.57
AMP-nitramine	2.27
PZ-nitramine	3.00

Mass spectrometric conditions:

Ionization: Agilant Jet Stream (AJS), negativ/positive ionizatino (switching)

Compound	**Parent-ion (m/z)**	**Product-ion (m/z)**
MEA-nitramine (negative)	105	46
MEA-nitramine (negative)	105	43
AMP-nitramine (negative)	133	61
AMP-nitramine (negative)	133	46
PZ-nitramine (positive)	132	86
PZ-nitramine (positive)	132	44

6. Quality assurance

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 analytes within the calibration range. The QC samples should follow all steps of the sample preparation procedure prior to analysis.

Method data (instrument parameters) should be stored routinely together with the sample data to verify the methodology and the method parameters used during analysis. Data (sample data and method parameters) should be collected and stored on a back-up file.

7. Results

Limits of detection are reported as signal with a signal-to-noise ratio better than 3 (S/N > 3). Overall LODs for the whole procedure of sampling, sample preparation and instrumental analysis are given in the table below.

Analyte group	***Analyte***	***LOD in 100X conc. condensate LLE extract (ng/L)***	***LOD in 100X conc. Condensate LLE extract[#] (ng/Nm^3)***
Nitramines	MEA-nitramine	25	1.25
	PZ-nitramine	1000*	50*
	AMP-nitramine	3	0.15

[#] Calculation based on an assumed condensate volume of 0.05L and a sampled flue gas volume of 1 Nm^3 (corresponding to approx. 1 hour sampling time).

* No concentrating step applied, direct injection.

8. Comments / critical factors:

A critical factor for sample preparation is the use of appropriate internal standards during extraction. As such, deuterated analogs are preferred. However these are at present not available for the nitramines in this procedure, and hence recovery using the unlabeled compounds must be used.

Solvent amines

1. Principle

Sample diluted to acceptable level if necessary and consequently analyzed with LC-MS/MS by direct injection

2. Interferences

High concentration of solvent amines will contaminate the instrumentation and therefore a dilution factor of at least 1 000 000 should be used for the first run for solvent samples.

3. Reagents and standards

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

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

Internal standards:
None

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

4. Equipment

Pipettes
Vials
Test tubes
Standard laboratory glassware
HP-UP/LC with MS/MS detector

5. Sample storage in laboratory

The samples should be analyzed as soon as possible after arrival to the laboratory.

Samples can be stored at +4°C for up to 2 weeks from time of sampling. If stored for longer periods than this, samples should be stored at -18°C

6. Pretreatment

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

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

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

7. Instrumental analysis

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

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

If UPLC available, the following conditions applies:

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

Alkylamines

1. Principle

Sample is injected to analysis vial and diluted with methanol to final consistency of 10 % methanol and analyzed by LC-MS/MS. Quantification is performed using external calibration curve with native standards.

Note: ***High concentration (over 0,5 %) of solvent amines may interfere with the analysis. Strongly alkaline conditions may lead to analyte loss due to evaporation.***

2. Reagents and materials

Laboratory equipment:

- Standard laboratory glassware such as Erlenmeyer flasks and beakers
- Balances with appropriate range and precision
- Pipettes
- Vials for sample extracts
- Millipore MilliQ water cleaning system or other UHQ water source

Reagents:

Solvents and reagents of sufficient purity shall be used, for example

- Methanol (Fisher Scientific (HPLC-grade) or equivalent)
- Acetonitrile (BDH Prolabo (LC-MS grade) or equivalent)
- UHQ water (Millipore or equivalent)
- Sulfamic acid

Standards:

High purity standards shall be used, for example

- Diethylamine (DEN), (Chem Service Inc.) O-2046, Purity 99,5 %
- Dimethylamine (DMA), (Acros Organics), 2M in methanol
- Ethylamine (EA), (Acros Organics), 2M in THF
- Methylamine (MMA), (AccuStandard Inc.) M-1666A-DI-R-ADD1, 2510 µg/mL (in water)
- Triethylamine (TEA), (Chem Service Inc.) O-297, Purity 99,5 %
- Trimethylamine (TMA), (Alfa Aesar GmbH & Co KG) H27324 33 % in ethanol

Mixture containing 10 mg/l of each component in methanol can be stored in freezer.

Internal standards (ISTD):
High purity standards shall be used, for example

- Diethylamine D10, (C/D/N Isotopes Inc.), D-2137, purity 98 %
- Triethylamine D15, (C/D/N Isotopes Inc.), D-1221, purity 98 %
- Methyl-d3-amine HCl (C/D/N Isotopes Inc.), D-279, purity >99 %
- Dimethyl-d6-amine HCl (C/D/N Isotopes Inc.), D-5090, purity 99%
- Trimethyl-d9-amine HCl (C/D/N Isotopes Inc.), D764, purity >99%

Mixture containing 10 mg/l of each component in methanol can be stored in freezer.

3. Sample storage in laboratory

The samples should be analyzed as soon as possible after arrival to the laboratory.

Samples can be stored at +4°C for up to 2 weeks from time of sampling. If stored for longer periods than this, samples should be stored at -18°C

4. Pretreatment

The total sample volume shall be measured with a suitable analytical balance. An aliquot of 900 µL is injected to vial, internal standards (in methanol) are added e.g. 50 µL of 1 mg/L solution and methanol is added to final volume of 1000 µL. If precipitation is observed the sample is filtered thru a disposable syringe filter (0.2 µm).
A spiked (standard addition at desired level) sample is added to the sample matrix.

5. Instrumental analysis

The UPLC conditions used are as followed:

- Ion source: ESI
- Column: Supelco Discovery® HS F5 (150 x 2.1 mm, 3 µm)
- Column temperature: 40 ºC
- Eluents: 0.02 % HCOOH in UHQ (A) and 0.02 % HCOOH in acetonitrile (B)
- Injection volume: 5 µL
- Flow rate: 0.4 mL/min
- Gradient 95/5 (A%/B%) for 5 min, 75/25 at 6 min, 30/70 at 12 min, 10/90 at 13 min and 95/5 at 14 min.
  Total run time 15 min

NOTE: ***Chromatographically complete separation of analytes is challenging and it is likely that some overlapping will occur.***

Standard stock solution will be prepared as 10 mg/L in methanol. External standards are diluted to the range of 10-500 µg/L. Calibration should be carried out with at least four calibration solutions. These solutions contain all native and all but one deuterated alkylamine standards in precisely defined amounts.

Analysis of samples is done with LC-MS/MS system and minimum of two transitions is monitored (excluding methylamine and methylamine D3):

- Diethylamine (DEN): 74,16 → 45,92 and 74,16 → 28,88
- Dimethylamine (DMA): 46,16 → 45,92 and 46,16 → 29,933
- Ethylamine (EA): 46,16 → 28,89 and 46,16 → 26,84
- Methylamine (MMA): 32,03 → 31,90
- Triethylamine (TEA): 102,22 → 73,95 and 102,22 → 57,91
- Diethylamine D10: 84,20 → 51,94 and 84,20 → 33,92
- Methylamine D3: 34,97 → 34,86
- Triethylamine D15: 117,30 → 64,89 and 117,30 → 85,03
- Trimethylamine D9: 69,03 → 49,00 and 69,03 → 51,03

6. Quality assurance

Blank sample will be treated and analyzed exactly as the actual samples. Standard addition to the sample matrix will be done with each sample set. Recoveries will be monitored.

Aldehydes

1. Principle

Underivatized samples (condensate from emission sampling, wash water up to 35 % solvent amines) are derivatizated using DNPH. Samples (incl DNPH-solutions from emission sampling) are further extracted with dichloromethane, solvent exchanged to acetonitrile and analyzed with UPLC-MS/MS or HPLC-UV.

2. Reagents and standards

LiChrolut EN 500 mg/6mL (Merck)
Acetonitrile (J.T. Baker or equivalent)
2,4-dinitrophenylhydrazine ≥ 99% (Sigma-Aldrich No. 42210-100G-F)
Dichloromethane (J.T. Baker (high purity) or equivalent)
2,4-DNPH-formaldehyde, 100 µg/mL, solvent acetonitrile, purity 99,9 % (Supelco No. 47177)
2,4-DNPH-acetaldehyde, 1 000 µg/mL, solvent acetonitrile, purity 99,9 % (Supelco No. 47340-U)

3. Equipment

Pipettes
Vials
Test tubes
Standard laboratory glassware
HPLC with UV-detector
Column: Waters Ltd. µBONDAPAK C18 10µm 125Å 3,9×300mm
UPLC with MS/MS detector
Column: Waters Acquity UPLC BEH C18 1,7 µm (2,1 x 100 mm)

4. Sample storage in laboratory

The samples should be analyzed as soon as possible after arrival to the laboratory.

Samples can be stored at +4°C for up to 2 weeks from time of sampling. If stored for longer periods than this, samples should be stored at -18°C

5. Pretreatment of underivatized liquid sample

Adjust pH of aqueous samples to 1.5 with 1M HCl.
Elute 5.0 mL of ACN and 10 mL of MQ-water through LiChrolut EN 500mg/6mL cartridge.
Elute 20 mL of 0.05 mg/mL DNPH-solution (derivatization solution) onto cartridge.
Add 50 mL of sample onto the cartridge.
Elute aldehyde derivatives with 7 mL of acetonitrile; send first 2 mL to waste.
Derivatized liquid sample
An aliquot of sample is weighed to separate container and extracted three times with dichloromethane. Depending on the concentration of the analytes either an aliquot of the dichloromethane phase is diluted into mobile phase or the dichloromethane is concentrated by evaporation and solvent exchanged to acetonitrile.

6. Instrumental analysis

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

HPLC conditions are as followed:

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

Analysis of samples can also be done with LC-MS/MS system with a minimum of two transitions is monitored:
Formaldehyde: 209,1597 → 151,044 and 209,1597 → 163,029
Acetaldehyde: 223,1596 → 151,142 and 223,1596 → 163,005

UPLC conditions are as followed:
Column: Waters Acquity UPLC BEH C18 1,7 µm (2,1 x 100 mm)
Column temperature 40 ºC
Eluents 0,02 % HCOOH in UHQ (A) and 0,02 % HCOOH in acetonitrile (B)
Injection volume 5 µL
Gradient 70/30 (A%/B%) for 1,5 min, 50/50 at 6 min, 0/100 at 10 min, 70/30 at 12 min.
Total run time 14 min

Ammonia

1. Principle

The determination of the ammonia is based on direct injection and quantification with external standards using HPLC-CD with IC column.

2. Reagents and materials

Laboratory equipment:

- Standard laboratory glassware such as Erlenmeyer flasks and beakers
- Balances with appropriate range and precision
- Pipettes
- Vials for sample extracts
- Water cleaning system, giving 18,2 MΩ water

Reagents:

Solvents and reagents of sufficient purity shall be used, for example

- Boric acid (Merck, No. 1.00165.1000)
- Nitric acid (J.T. Baker 69.0-70.0 % or equivalent)

Standards:

High purity standards shall be used, for example

- Ammonium chloride (Merck, No. 1.01145.0500 >99,8 %)

3. Sample storage in laboratory

The samples should be analyzed as soon as possible after arrival to the laboratory.

Samples can be stored at +4°C for up to 2 weeks from time of sampling. If stored for longer periods than this, samples should be stored at -18°C

4. Pretreatment

The sampling absorbent is transferred into a volumetric flask and the sampling container is washed with UHQ-water.
The sample is diluted to known volume and an aliquot of it is placed into an LC-vial.

5. Instrumental analysis

IC or HPLC apparatus with the following conditions:

- Column: Dionex IonPac CS14 x 250 mm (or Dionex IonPac CS16)
- Detector: Conductivity detector with (or also possibly without) a suppressor
- Column temperature: min. 65 ºC
- Eluent: Nitric acid 3 mM in UHQ-water
- Injection volume: 20 µL
- Isocratic conditions

Calibration:
External calibration will be used for quantification. Reference stock solution of ammonium ion is prepared by diluting approximately 0.3 g dried ammonium chloride into a small volume of UHQ-water and diluting it into 100 mL with UHQ-water. The ammonium ion concentration in stock solution is roughly 1 g/L but exact concentration must be calculated. Standards are prepared by diluting the stock solution with suitable amounts of water. Typical standard concentrations are between 5-100 mg/L

6. Quality assurance

Recoveries of standard additions and blank values are monitored.
LOQ is between 5 mg/L and 15 mg/L depending on the amount of near-eluting monoethanolamine in the sample.

7. Overall method uncertainty

As the method is based on direct injection, analytically the errors are derived from possible dilution steps, repeatability of the instrument and matrix effects. Instrument repeatability shall be resolved and multiple standard additions shall be done to actual sample matrix.