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SUBTASK2
PROCEDURES FOR MANUAL SAMPLING

SUBTASK2
PROCEDURES FOR MANUAL SAMPLING

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SUMMARY

In the sub-task 2 the aim was to find out the most suitable methods for CCS plant emission gas manual sampling in order to analyze amine and other related compounds. The compound groups were nitrosamines, alkyl amines, solvent amines, amides, aldehydes and ammonia. Many of the methods found in the literature survey were standard methods i.e. by NIOSH and OSHA but also multiple article methods were found. The methods were evaluated in order to find suitability for the intended purpose and the fully validated standard methods were favored.

Even though multiple sampling methods were available, none of them was directly suitable for flue gas sampling but for the air sampling and the methods need to be adjusted for flue gas. The methods consisted of different sampling systems, mainly impingers and other liquid phase sampling systems and variety of solid sorbent materials.

It was found that sampling of the compounds form different groups with the same method is not possible. One reason is the susceptibility for decomposition. For example nitrosamines are prone to photodegradation, especially in acidic environment. Some congruent sampling materials were also found, i.e. XAD-2 resin seems to be suitable at least for amine and aldehyde sampling.

The sampling method should be integrated with the analytical method since both of them are more or less dependent of each other. Thus the method suitability can not be evaluated by paper only but some testing is expected to be required. Since the analysis method development (sub-task 5) is not ready yet, the final selection of the sampling method cannot be done. However, some of the most used sampling methods according to the literature survey have been presented.

Besides the sampling materials, other factors related to reliable sampling that should be taken account are the need for isokinetic sampling, heating of the sampling system (or part of it) and the materials in contact with the samples (should be inert).

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FIGURES

1. TERMS AND DEFINITIONS

The list of used abbreviations is given below:

AMP	2-Amino-2-methyl-1-propanol
CCS	Carbon Capture and Storage
DEA	Diethanolamine
DEN	Diethylamine
DMA	Dimethylamine
Dnpz	1,4-Dinitrosopiperazine
EA	Ethylamine
EDA	1,2-Diaminoethane
IPA	Isopropylalcohol
MDEA	N-Methyldiethanolamine
MEA	Monoethanolamine
MMA	Methylamine
n	normal state (101.3 kPa, 0 °C, dry gas)
NDEA	N-Nitrosodiethylamine
NDELA	N-Nitrosodiethanolamine
NDMA	N-Nitrosodimethylamine
NMOR	N-Nitrosomorpholine
NOC	N-Nitrosorganic Compound
NPIP	N-Nitrosopiperidine
ppb	parts per billion (10^{-9})
ppm	parts per million (10^{-6})
SVOC	Semivolatile Organic Compound
TEA	Triethylamine
TMA	Trimethylamine

2. FOREWORD TO THE DRAFT

This draft report is updated version for the draft report send at 15.9.2010. The report contains main information about the literature survey and some preliminary conclusions. Implementation between analysis method developed and sampling system presented is expected to focus during sub-task 5. Thus, if some updates for the sub-task 2 appear later on (during sub-task 5) the information will be amended on the sub-task 5 report. Updated information is also expected for the final sub-task 2 report.

3. INTRODUCTION

This technical document will explore analysis methods for the compounds presented at the Table 3. The matrix is exit gas after the CCS-plant flue gas demister.

The scope is merged to the analysis methods presented at the sub-tasks 4 and 5. All brands are presented as examples if not noted otherwise.

At the time written method development of the analysis is in progress. Many details are still open and will be added to the sub-task 5 report.

Scope of work:

- Basic information of the project related to the current report
- Literature survey
- Evaluation of the presented sampling methods
- Design of the sampling equipment
- Calculated estimation of break through volume/sampling time
- Practices during sampling
- Quality management
- Estimation of overall uncertainty, repeatability and reproducibility of sampling

4. MATRIX AND STUDIED COMPOUNDS

4.1 Delivered information

At the time the report was established detailed information about the CCS-plant was not available. Delivered estimation of flue gas properties is delivered by the company and presented at the Table 1. The flue gas conducted to the CCS-plant is from natural gas fired gas turbines so the sulphur dioxide and dust concentration on the flue gas is estimated to be negligible.

Table 1 Delivered process parameters for the flue gas

	Unit	Large scale plant	Pilot plant
Gas flow gas rate	million Sm^3/h	700 000 - 2 300 000	250-1200
Temperature	°C	25-50	25-50
Moisture		saturated probably with droplets	saturated probably with droplets
Pressure		± outside pressure	± outside pressure
Main body velocity	m/s	2-3	2-3
Gas velocity at pipe exit	m/s	About 20	2-3
Composition			
- oxygen, O_2	mol-%	15	15
- nitrogen, N_2	mol-%	81.5	81.5
- carbon dioxide CO_2	mol-%	0.5	0.5
- water, H_2O	mol-%	3	3
- amines	ppm	< 5	< 5
- ammonia, NH_3	ppm	< 50	< 50
- NO_x	ppm	n/a	n/a
- NO_2	ppm	n/a	n/a
- SO_2	ppm	low	low
- dust	mg/m^3n	low	low

The treated flue gas coming from the absorber tower undergoes water wash before being emitted to the atmosphere. The water wash reduces the emissions of process amines and other undesirable compounds. The sample will consist mostly of water. Process amines and their degradation products will be present in trace amounts. Regardless, process amines are estimated to be remarkable factor on flue gas sampling and analysis. Examples of possible solvents are presented at Table 2.

Table 2 Examples of aqueous solvents

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

4.2 Compounds of interest

Compounds of interest are process amines or degradation or transformation products of process chemicals and flue gas. The compound of interest and their properties are presented at Table 3.

Table 3 Compounds of interest

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

Compound	**CAS-number**	**Formula**	**MW (g/mol)**	**T_b (°C)**	**Water solubility**	**Reference**
MEA	141-43-5	C_2H_7NO	61.08	171	miscible	(Verschueren 2001, Wypych 2008)
Piperazine	110-85-0	$C_4H_{10}N_2$	86.14 (anhydr.)	146 (anhydr.)	soluble 150 g/l at 20°C and pH 12	(Bingham et al. 2001, Institute for Health and Consumer Protection European Chemicals Bureau. 2005)
Amides						
Acetamide	60-35-5	C_2H_5NO	59.1	222	2 000 g/l	(Wypych 2008)
Formamide	75-12-7	CH_3NO	45.04	210	infinite / miscible	(Verschueren 2001, Wypych 2008, Dean 1999)
Aldehydes						
Acetaldehyde	75-07-0	C_2H_4O	44.06	21	infinite	(Wypych 2008)
Formaldehyde	50-00-0	CH_2O	30.03	-21 (gas)	soluble, 400 g/l	(Wypych 2008)
Others						
Ammonia	7664-41-7	NH_3	17.03 (anhydr.)	-33 (gas)	600 g/l (15 °C)	(MSDS 2005)

*Priority compounds

5. LITERATURE SURVEY OF THE AVAILABLE METHODS

5.1 Introduction

The focus on literature survey was to find appropriate sampling methods for the compounds presented at the Table 3. The findings are presented below.

5.2 Materials for sampling

Sampling of gases and vapours is often performed using sorbent tubes, impingers of collection bags (McDermott 2004). Also stainless steel canisters and cryogenic traps have been employed in sample collection. Canisters are used for very low levels of volatile organic compounds while cryogenic methods are used to collect highly volatile or otherwise difficult compounds which are hard to get stabilized on sorbents. Solid sorbent sampling and impinger samplers were considered to be the most usable for the indented use and are presented below.

5.2.1 Solid sorbent sampling

In solid sorbent sampling (activated) charcoal (carbon), silica gel (amorphous form of silica, recommended for amines), polymeric polymer sorbents and molecular sieves have been widely used (McDermott 2004). Solid sorbents are specific for compound or groups of compounds and one sorbent will not work with all compounds. Most solid sorbents are of non-selective nature thus also unwanted compounds are possibly sampled. The nomenclature of the sorbent types is not standardized and for example widely used XAD is just a brand name by manufacturer. The sorbent have only certain number of active sites, thus when there are multiple compounds present the amount of any individual compound that can be collected will be reduced. The most concerning problem when working with sorbent tubes is the occurrence of breakthrough. Breakthrough occurs when the front section of a tube is saturated and enough compounds accumulate in the backup section causing the compounds to exit the tube with the airstream.

When selecting sorbents the potential for water absorption must be taken into account. Competition for the adsorbent’s active sites might occur between the compound being sampled and water resulting in breakthrough with lower amounts. Other important factors are sampling temperature, sampling flow rate and later on the detection method. Some sorbent tubes such as Tenax can be connected to analytical devices such as GC-MS without additional steps between. Characteristics of some solid sorbents are presented at Table 4.

Table 4 Characteristics of some solid sorbents (McDermott 2004)

Solid sorbent	Characteristics
Activated carbon	• Very large surface area:weight ratio • Reactive surface • High absorption capacity • Non-polar compounds preferred • Might be affected by high humidity • Rather non-selective • Compound desorption might be difficult
Silica gel	• Less reactive than activated carbon • More selective than activated carbon • Desorption easier than from activated carbon • Polar in nature • Higher polarity compounds displace lesser polarity compounds • Very hygroscopic, humidity might decrease the absorption efficiency (water might displace collected components)
Porous polymeric sorbents (e.g. Tenax and XAD materials)	• Less surface area and less reactive surface compared to activated carbon • Absorption capacity and reactivity is lower than of activated carbon • Sometimes irreversible adsorption of e.g. amines • CO_2 might displace less volatile compounds • Thermal instability
Molecular sieves	• Water may displace organic compounds • Mainly for highly volatile non-polar organic compounds

Activated carbon is considered to be the most common solid phase extraction material used for analysis of nitrosamines in water (Padhye et al. 2010). However, under ambient aerobic conditions activated carbon materials can catalyze transformation of secondary amines into trace levels of nitrosamines.

Alumina gel and florisil are sorbents occasionally used in integrated gas and vapour sampling (McDermott 2004). Alumina gel is a form of aluminium oxide and used in special application for polar and higher molecular weight compounds. Florisil is based on silicic acid and used for example in nitrosamine sampling (OSHA 6, OSHA 13, OSHA 17).

5.2.2 Impinger samplers

The function of the impingers is to provide sufficient contact between the sampled air and the liquid surface to provide complete absorption of the gas or vapour. Impingers are suitable for sampling of non-reactive gases and vapors that are highly soluble in the absorbing liquid (such as HCl) as well as for those that react rapidly with a reagent in the solution. Originally impingers were primarily used for aerosol collection, but the current applications are for gas and vapour sampling. The midget impinger is designed to contain 10 – 20 ml of liquid and they are usually made of glass. Variations of the basic midget impinger have been developed including for example membranes.

5.3 Nitrosamines

When finding information for the literature survey it appeared that sampling of nitrosamines are mainly performed from ambient or workplace air. Publications or standards related to emission measurements or wet flue gas sampling was not found.

Nitrosamines are sensitive to photodegradation thus care must be taken not to expose them to sunlight (Goff 1983; OSHA 27). Storage of the samples is therefore a critical point in the analysis of nitrosamines, both for gas and liquid samples. Amber glass vials with PTFE-lined caps are often the containers of choice for water samples containing nitrosamines. If preserved in the dark, samples are suspected to be stable especially if refrigerated (Munch & Bassett 2004; Goff 1983). It was observed that refrigerated NDMA extract concentrates showed minimal NDMA loss after 6 months storage when refrigerated in dark (NIOSH 1994i, Cheng et al. 2006). Nitrosamines may be present in trace amount in rubber products; therefore samples might be contaminated from repeated injections from autosampler vials with PTFE-coated rubber septa (Munch & Bassett 2004). When sampling air for nitrosamines, it is fundamental to be certain that nitrosamines are indeed present in the original sample and not formed on the sampling device in presence of nitrosating agents.

Different sampling mediums are applied to the nitrosamine sampling. Commercial Thermosorb/N cartridges are designed to especially for nitrosamine sampling (**NDMA, NDEA, NDPA, NDBA, NPIP, NPYR, NMOR**) (OSHA 27). Sampling and analysis of the compounds are validated at workplace air matrix by OSHA (OSHA 27). Validated flow rate in sampling is 0.2 to 2 l/min. Minimum sample volume is 15 l at 10 µg/m³ with maximum of 1 000 l. The manufacturer reports that 1500 µg of N-nitrosamines may exceed the capacity of a single tube. For the higher concentrations, tubes could be connected parallel. Breakthrough volume of Thermosorb/N tubes is sensitive to humidity. When the relative humidity is decreased from 80 %, the 5 % breakthrough air volume for NDMA was found to increase.

The commercial ThermoSorb/N N-nitrosamines air sampler is constructed to prevent the in situ formation of N-nitrosamines from airborne precursors. The manufacturer has tested the sampling device for the artifactual formation of NDMA, NPYR, NMOR and diisopropylnitrosamine using 50 µg each of the respective precursor secondary amines and nitrogen oxides (NO_x). The amines were spiked on the ThermoSorb/N tubes and then 100 l of air containing 0.2, 0.5, 1, 2 or 4 ppm NO/NO2 at a 1/1 ratio was sampled. Various untreated solid adsorbents formed the N-nitrosamines quite easily but at these levels of amines and NOx, the ThermoSorb/N cartridges were shown to be artifact-free (OSHA 27).

It should be noted that NO_x concentration used on the previous study is about 10 times lower than on the exit gas of ordinary gas turbine. CCS-process will capture NO_x compounds and exit gas concentration may be at the same level than study above. It is still unknown if there are other potential interferences with the collection of N-nitrosamines using ThermoSorb/N cartridges. Effect of CO_2 is unknown.

The sample is stable in ThermoSorb/N tubes when stored at ambient temperatures for at least 17 days (OSHA 27).

NDELA is considered to be a non-volatile nitrosamine and if the airborne compound is present, it is probably contained in an aerosol. Since the collection efficiency for aerosols on solid sorbents has not been established, the alternative air sampling devices are filters and bubblers (OSHA 31). NDELA samples are taken to Gelman Type A glass fiber filters in open-face cassettes (OSHA 31). Recommended air volume is 480 l and sampling rate 2 l/min.

Nitrosamines are stable at neutral or alkaline solutions, but less stable in acidic conditions (Bingham et al. 2001). In addition, nitrosamines are rapidly photodecomposed (with initial cleavage of the N-N bond) in dilute acid solutions, but are relatively stable to light in neutral solutions (Kearney 1980). It is also generally believed that nitrosamines are rapidly decomposed by light in the vapor phase. For example the half-life of NDPA in air is estimated to be about 20 minutes under cloudy conditions and 10 minutes in bright sunlight. In addition, nitrosamines are subject to oxidation, reduction, alkylation, condensation, and other types of reactions with appropriate reagents. This is important not only for preservation step, but at possible sampling with alkylamines. Some sampling methods for nitrosamine compounds are presented at Table 5.

5.3.1 Sampling methods for nitrosamines

Table 5 Sampling methods for nitrosamines

Matrix	Compound	Method type	Absorbent	Sampling rate	LOD	Characteristics	Maturity/Ref
vulcanization fumes	NMOR specific	Q	**Wet absorption** of the air samples through a solution of: 30 ml IPA, 0.001 M KOH + internal standard (N,N-dimethyl aniline). Absorption unit cooled on methanol path and dry ice (-20 °C)	0.12 - 2 l/min 40-240 min	10 pg in 1 µl	NMOR concentrations 99.5 to 0.0098 µg/ml. Linear response. Applicable also to other volatile nitrosamines.	Low maturity: Article (Aarts et al. 1990)
workplace air	Mixture of volatile N-nitrosamines NDMA, NDEA, NMOR, NPIP	S, Q	**Sorbent adsorption onto Thermosorb/N tubes**	n/a	2 ng in 1 µl	Within-day overall standard deviation of the retention times was within 2 sec over a concentrated range of 0.02 to 2 ng/µl.	Low maturity: Article (Cooper 1987)
air	Mixture of NDEA, NDMA	Q	**Collection** on two Florisil adsorbent tubes (pretreated with 11 mg of DL-α-tocopherol) in series	25 l @ 0.2 l/min	0.4 µg/ m^3, based on recommended air volume.	Average desorption of NDEA was 95.3 %. Humidity reduces the adsorption of the amines on the adsorbent.	High maturity: OSHA method 13, fully validated (OSHA 13) OSHA method 6, fully validated (OSHA 6)

Matrix	Compound	Method type	Absorbent	Sampling rate	LOD	Characteristics	Maturity/Ref
air	Mixtures of volatile nitrosamines in air. NDMA, NDEA, NPIP, NMOR.	Q	**Collection** by absorption on ThermoSorb/N air samples	75 l @ 0.2 - 2 l/min	Overall procedure based on recommended air volume. NDMA 0.13, NDEA 0.13, NPIP 0.12 and NMOR 0.2 µg/ m^3	Sensitivity of the analytical procedure (area units per µg/ ml): NDMA 239864, NDEA 208144, NPIP 179720, NMOR 176596. Recovery of the analytes from the collection medium (%):NDMA 97.4, NDEA 99.7, NPIP 96, NMOR 98.1. Precision of the analytical method only (pooled coefficients of variation): NDMA 0.037, NDEA 0.044, NPIP 0.051, NMOR 0.032.	High maturity: OSHA method 27, fully validated (OSHA 27)
air	NMOR specific	Q	**Collection** by two sampling tubes (Polar Partition and Florisil, both coated with ascorbic acid) connected in series.	40 L @ 0.2 L/min	0.4 µg/ m^3. Reliable quantitation limit: 0.6 µg/ m^3.	Average recovery: 96.3% for treated Florisil tubes and 96.7% for treated Polar Partition tubes. Light protection, storage in freezer.	High maturity: OSHA method 17, fully validated (OSHA 17)
ambient air	Mixture of volatile nitrosamines NDMA, NDEA, NMOR, NPIP	Q	**Collection** on ThermoSorb/N solid sorbent tube.	0,.2-2 l min: 15 l @10 µg/m^3 max: 1000 l The working range is 0.003 to 10 mg/m3 for 50 l air sample	0.05 µg per sample. (Injection volume 5 µl).	TEA is very specific for N-nitroso compounds; therefore there is little or no interference from other co-eluting compounds. Desorption efficiency: nearly 100 % for all the studied nitrosamines. Method evaluated in the range 0.05 to 0.5 µg.	High maturity: NIOSH Method 2522 (NIOSH 1994i)

Matrix	**Compound**	**Method type**	**Absorbent**	**Sampling rate**	**LOD**	**Characteristics**	**Maturity/Ref**
ambient air	Volatile nitrosamines in industrial ambient air. NDMA, NMOR.	Q	**Collection** on ThermoSorb/N cartridges.		0.05 µg/ m^3per 100 l of air.		Low maturity: Article (applicative) (Monarca et al. 2001)
ambient air	Volatile nitrosamines NDMA, NDEA, NMOR.	Q	**Collection** on ThermoSorb/N cartridges preceded by ascorbic acid-impregnated Teflon filters. **Elution**: 33% MeOH in chloroform, 10 % chloroform in DCM.			Recovery %: NDMA 93 ± 2, NDEA 95 ± 7, NMOR 94 ± 5. Sensitivity: 10 pg/injection for NDMA, 14 pg/injection for NDEA.	Low maturity: Article (Mahanama & Daisey 1996)
air	NDELA specific	Q	**Collection** using Gelman Type A glass fiber filters in open-face cassettes. **Extraction** with 2-propanol and ion exchange resin (Dowex 1-X8, 20-50 mesh).	480 l @ 2 l/min	0.42 µg/ m^3 based on recommended air volume.	Reliable Quantitation Limit (RQL) 0.42 µg/ m^3. Recovery (average) 99.8 %, confidence limits 95 %. Sensitivity 121.907 (area units per µg/ ml).	High maturity: OSHA method 31 (OSHA 31). Fully Validated.
atmospheric samples	Nitroso organic compounds (NOC)	G	2.5 µm virtual impactor, 47 mm quartz fiber filter, 50 ml XAD-II resin	72 h @ 170 l/min	0.8 pmol	Excellent selectivity for NOC (only interference nitrates). Water does not interfere. Possibly applicable also to water samples. Quartz filter – XAD-II resin suffer significant artifactual formation of NOC	Low maturity: Article (Ding et al. 1998)

5.3.2 Evaluation of methods for nitrosamine sampling

N-nitrosamines can be divided into volatile (NDEA, NDMA, NMOR and NPIP) and non-volatile (N-nitrosopiperazine, NDELA) nitrosamines. The K_{oc} and K_{ow} values for the specific nitrosamines are presented at Table 6. Different sampling methods are estimated at the Table 7.

Table 6 K_{oc} and K_{ow} of nitrosamines

Compound	K_{oc}	K_{ow}
NMOR	n/a	0.36
NDEA	43	3.02
Dnpz	n/a	n/a
NDMA	12	0.27
NDELA	n/a	n/a
NPIP	n/a	22.9
N-Nitrosopiperazine	n/a	n/a

Table 7 Different sampling approaches for nitrosamine sampling

Method	Advantage	Disadvantage
Cold traps in series (-95…-79 C)		The cold traps are difficult to maintain and are reported to enable the artifactual formation of NDMA from precursor amines and nitrogen oxides (Fisher 1977)
Ambient temperature KOH bubblers	Free of artifact formation, may be suitable for the flue gas sampling.	Retention efficiency decreases with increasing sampling time and temperature (Rounbehler 1980).
Tenax GC, solid sorbent	Allows thermal desorption, high thermal stability (McDermott 2004). Relatively inert and low affinity for water vapor.	Tenax GC has a relatively low breakthrough volume for NDMA ((Rounbehler 1980, McDermott 2004). May concentrate precursor amines and nitrosating agents resulting in artifactual in situ formation of the analyte (Rounbehler 1980). Used mostly for low concentrations of VOCs. Tendency to decompose during sampling. Not effective for LMW hydrocarbons and mid-range (C_{5-12}) highly polar compounds.

Activated carbon-water suspension	May be suitable for the flue gas sampling.	May concentrate precursor amines and nitrosating agents resulting in artifactual in situ formation of the analyte (Rounbehler 1980). Nitrosamine formation from secondary amines possible (Padhye et al. 2010).
Vitamin E and C treated Florisil adsorbent tubes	The vitamin E and C treated Florisil adsorbent tubes were shown to be artifact resistant.	Nitrosamines were reported to be less stable in acidic conditions (Kearney 1980).
XAD-4 resin	May be suitable for the flue gas sampling. High sorption capacity.	May concentrate precursor amines and nitrosating agents resulting in artifactual in situ formation of the analyte. Known artifact formation (Rounbehler 1980).
ThermoSorb/N	Free of artifact formation. The sampling and analytical procedures permit the simultaneous determination of a mixture of analytes The samples are stable when stored at ambient temperatures for at least 17 days.	Commercial availability The ability of the sampling device to collect and retain the analytes is limited. The process by which the ThermoSorb/N tubes prevent artifact formation is proprietary and possible side effects or capacity on flue gas sampling is unknown.

According to the literature survey (Table 5) the most used method (also by OSHA and NIOSH) is Thermosorb/N cartridges. Also vitamin E and C treated Florisil adsorbent and Gelman Type A glass fiber filters are suitable for nitrosamine sampling according to OSHA. However, since the methods presented were not for emission measurements or wet flue gas sampling, the method suitability is not clear. The concentrations in flue gas are much higher and also the excess of distractive compounds and humidity etc. is higher, which should be considered when planning the suitability of a sampling method. Thus, testing of the methods to find out the actual suitability for the flue gas sampling is expected to be required.

5.4 Alkylamines

As in the case of nitrosamines it appeared that sampling of alkylamines is mainly performed from ambient or workplace air. However, one measurement was published about the emissions in a compost treatment plant (Maris et al. 1999). Other publications or standards related to emission measurements or wet flue gas sampling was not found.

Different sampling methods are based on percolating through the acidic (e.g. HCl, H_2SO_4, phosphoric acid) liquid or acid coated sample resins (XAD-2, XAD-7) or filters, silica gel grains or direct derivatization onto SPE cartridges (Table 8).

Degradation of alkylamines is not reported. On the contrary to nitrosamines, alkylamines can be sampled onto acidic solutions.

5.4.1 Sampling methods for alkylamines

Table 8 Sampling methods for alkylamines

Matrix	Compound	Method type	Absorbent	Sampling rate	LOD	Characteristics	Maturity/Ref
air	MMA, DMA, EA, DEN and other aliphatic and aromatic amines.	Q	Pre-concentration by percolating the air samples through a 0.1 M HCl solution	46 ml/s (1 m^3 of air in about 6 h). Air samples 0.5–1.5 m^3	0.08-0.01 ng/m^3	Recovery 75.6 – 96.8 %,	Low maturity: Article (Akyuez 2007)
air	TMA, TEA, specific.	Q	XAD-7 resin coated with 10 % phosphoric acid. Desorption with 1:1 MeOH: deionized water solution. Dilution in 1.0 N NaOH: MeOH solution.	10 l at 0.1 l/min (maximum 20 liters at a flow rate of 0.2 l/min)	0.05 mg/m^3. Reliable quantitation limit: 0.08 ppm (0.2 mg/m^3) TMA 0.04 ppm (0.2 mg/m^3) TEA	Desorption efficiency: 98.9 % TMA, 99.9 % TEA. Retention efficiency: 101 % TEA, 99.1 % TMA. Good storage stability of the samples.	Medium maturity: Partially validated OSHA method PV2060 (OSHA PV2060)
dry air	DMA, DEN, specific	Q	Sampling onto silica gel filled tube. Desorption with H_2SO_4 in aqueous MeOH and neutralization of the extract with KOH (pH>10).	0.01 to 1.0 l/min (Volume min. 3 l, max. 30 l)	0.02 mg/sample.	The working ranges for 20-L air samples were 8 to 183 ppm (25 to 550 mg/m^3) for DEN and 4 to 71 ppm (7.5 to 130 mg/m^3) for DMA. Overall accuracy18.7 % DEN, 13.2 % DMA. Method evaluation only in dry air. Silica gel may have a reduced capacity at high humidity. The MeOH peak could interfere in low-level analysis. A nitrogen-specific detector instead of FID will increase sensitivity. Shipment as refrigerated.	High maturity: NIOSH method 2010 (NIOSH 1994c)

Matrix	Compound	Method type	Absorbent	Sampling rate	LOD	Characteristics	Maturity/Ref
ambient air in presence of rubber or air above a bacterial culture	MMA, DMA, TMA, EA, DEN, TEA, and other volatile primary and secondary amines	S	Sampling onto XAD-2 impregnated with 1-naphtylisothiocyanate (NIT) that is the derivatization agent. Extraction of the derivatives with acetonitrile.		0.12-0.25 ng/μl		Low maturity: Article (Claeson et al. 2004)
air	DEN, DMA, EA, MMA, TEA, TMA. Primary, secondary and tertiary amines	Q	Two different sampling techniques studied: sampling tubes for direct sampling and axial badge type samplers for diffusive sampling. Phosphoric acid impregnated glass wool or fibers were used in both sampler types. Elution with high purity water and filtration.		DEN 12, DMA 121, EA 108, MMA 57, TEA 8, TMA 23 pg/μl. In air: DEN 120, DMA 1210, EA 1080, MMA 570, TEA 80, TMA 23 ng/m^3.	Diffusive sampling. RSD 9.9% Limit of quantification LOQ (pg/ μl): DEN 46, DMA 543, EA 425, MMA 167, TEA 29, TMA 77. Samples were stable in storage for 60 days. The recovery % was studied.	Low maturity: Article (Rampfl et al. 2008)
ambient air	MMA, DMA and alkanolamines DEA and MEA. Other primary and secondary low molecular weight amines	Q	Sampling with glass fiber cassettes treated with H_2SO_4 in MeOH. Elution and derivatization with dansyl chloride in acetonitrile and water (dansylation). The products of dansylation are fluorescent aromatic sulfonamides.	1 l/min for 15 min	LOQ (external calibration): DEA 0.09, MEA 0.05, MMA 0.02, DMA 0.07 μg/ml	Recovery was close to 100 % for all the amines. LOQ and sensitivity for internal calibration are also given.	Low maturity: Article (Fournier et al. 2008)

Matrix	Compound	Method type	Absorbent	Sampling rate	LOD	Characteristics	Maturity/Ref
air	MMA, EA, DEN Specific for each amine.	Q	Sampling onto XAD-7 resin coated with 10 % (w) NBD chloride. Desorption with 5 % (W/v) NBD chloride in tetrahydrofuran (small amount of bicarbonate present).	0.2 l/min (10 l)	LOD and Reliable quantitation limit: 28 ppb (35 μg/m^3) MMA, 16 ppb (29 μg/m^3) EA, 53 ppb (160 μg/m^3) DEN	Target concentration: 10 ppm. Standard error of estimate at the target concentration: 5.8 % MMA, 8.0 % EA, 7.1 % DEN Recovery %: MMA 97, EA 87, DEN >91	High maturity: Fully validated OSHA methods 40 (MMA), 36 (EA), 41 (DEN) (OSHA)
air	DMA Specific	Q	Sampling onto XAD-7 resin coated with 10 % (w) NBD chloride. Desorption with tetrahydrofuran (small amount of bicarbonate present).	0.2 l/min (10 l)	LOD and Reliable quantitation limit: 24 ppb (43 μg/m^3) DMA,	Target concentration: 10 ppm (18 mg/m^3). Standard error of estimate at the target concentration: 5.5 % DMA, Recovery %: DMA>93	High maturity: Fully validated OSHA method 34 (OSHA 34)
air	MMA, DMA,DEN, and other aliphatic amines	Q	Sampling onto silica gel, washed with H_2SO_4 : acetonitrile (1:1), pH adjusted to 10 with 1.1 N NaOH.	400 ml/min, 4h	24 ppb MMA, 60 ppb DEN	Recovery MMA 95.6%, DMA 90.3%, DEN 91.0%. Range of validation: 15-47 ppm. Quantitations from 0.02 to 0.38 mg/m^3 air. Sampling temp. 26 or 28 °C.	Low maturity: Article (Gao et al. 1990)

Matrix	Compound	Method type	Absorbent	Sampling rate	LOD	Characteristics	Maturity/Ref
ambient air	DMA mainly. Other amines: MMA, EA, DEN and mixtures.	S/ Q (only to DMA. Interferences by NH_3, primary amines and DEN tested)	Sampling onto C_{18} SPE cartridges. Derivatization inside the cartridges with 1,2-naphtoquinone-4-sulfonate. Desorption with water: acetonitrile (1:1, v/v).	15 min at 30ml/min	DMA 2, MMA 9, EA 17-21, DEN 11-10 µ/g	Sampling temp. was 24.5 °C and relative humidity 45%. Useful if a high number of samples must be processed (rapid, low-cost, suitable for the field). Distinction between primary and secondary amines possible by visual observation. Satisfactory linearity and precision obtained. Efficiency %: MMA 97, EA 84, DMA 97, DEN 82.	Low maturity: Article (Moliner Martinez et al. 2004)
emissions in a compost treatment plant	MMA, EA, DMA, DEN, TMA, TEA, and other C_1-C_4 aliphatic amines	Q	Absorption samples in an HCl solution		0.2 µg/l, for secondary and tertiary amines 10 µg/l for primary amines	The column needs systematic addition of ammonia to the sample in order to obtain good repeatability. RSD = 0.6-6.4 %. Primary amines were detected from 10 to 3000 mg/ l.	Low maturity: Article (Maris et al. 1999)

5.4.2 Evaluation of methods for alkylamine sampling

Evaluation of sampling methods is presented at Table 9.

Table 9 Different sampling approaches of alkylamine sampling

Method	Advantage	Disadvantage
XAD-2 and XAD-7 resins	May be suitable for the flue gas sampling. Good storage stability of the samples (OSHA PV2060). Good sorption capacity.	May concentrate precursor amines and nitrosating agents resulting in artifactual in situ formation of the analyte. Known artifact formation.
Silica gel	Relatively selective (McDermott 2004).	Silica gel may have a reduced capacity at high humidity(McDermott 2004).
Phosphoric acid impregnated glass wool	Good sample stability (up to 60 days in storage) (Rampfl et al. 2008).	Used only with diffusive sampling. Might not be usable for the flue gas sampling (Rampfl et al. 2008).
Glass fiber cassette	Derivatization can be done during elution (Fournier et al. 2008). Good recovery, fast flow rate, could be suitable for high temperatures.	
C_{18} SPE cartridge	Rapid, low-cost, suitable for the field (Moliner Martinez et al. 2004).	Low recovery for some compounds, sorbent should not get dry (Perez-Magarino et al. 2008).
HCl solution	Cheap, analysis can be performed as for waters.	

Only one measurement besides the ambient/workplace air sampling was presented in literature. When measuring emissions in a compost treatment plant, absorption of samples in HCl solution was used (Maris et al. 1999). HCl absorption might be a usable method for sampling. Multiple methods by OSHA recommend also XAD-7 resins for sampling (OSHA methods PV2060, 34, 36, 40, 41). Suitability of the ambient air sampling methods should be tested prior to final selection of the method.

5.5 Solvent amines

Solvent amines have also mainly been sampled from ambient air and less in emissions (Table 10). The following sampling materials have been employed: XAD-2 and XAD-4 resins, silica gel, glass fibre cartridges and impinger (15 ml of 2 mM hexanesulfonic acid).

5.5.1 Sampling methods for solvent amines

Table 10 Sampling methods for solvent amines.

Matrix	Compound	Method type	Adsorbent	Sampling rate	LOD	Characteristics	Maturity/Ref
ambient air	MEA	Q	XAD-4 resin coated with cyclohexanone as derivatization agent. Desorption with MeOH.	0.2 l/min (20 l)	1µg	Relative humidity 45%. Stable derivatives: collected samples were stable ≥ 2 weeks. Working range: 0.5 – 20 mg/m^3 in a 10 l air sample. Recovery of MEA from the tubes: 88 - 98 %. Other **aliphatic amines and NH$_3$** can be collected and quantified on the same tube.	Low maturity: Article (Gaind et al. 1992)
air of industrial premises	MEA	Q	Sampling with film chemisorption tubes in acid conditions (sulfuric acid). Condensation of the sample with benzaldehyde (2-phenyloxazolidine).	0.5 l/min (10 l)	Estimated 0.2 mg/m^3	Interferences: NH$_3$ and other amines that react with H$_2$SO$_4$ and decrease the chemisorption capacity of the tube. In particular, DEA and TEA.	Low maturity: Article (Zenkevich & Chupalov 1996)
working atmosphere	Piperazine specific	Q	Two-phase derivatization with ethyl- or isobutyl chloroformate in presence of NH$_3$. NH$_3$ insured a quantitative recovery.				Low maturity: Article (Skarping et al. 1986)

Matrix	Compound	Method type	Adsorbent	Sampling rate	LOD	Characteristics	Maturity/Ref
air	AMP specific	Q	Sampling on glass tubes containing XAD-2 resin coated with 10 % (w/w) 1-naphthylisothiocyanate (NITC). NITC works as derivatization agent forming a stable derivative. Extraction with dimethylformamide.	0.1 l/min (10 l)	Overall 0.04 ppm based on 10 l air volume.	Target concentration 3 ppm (11 mg/m^3). Desorption efficiency from sampling tubes mean of 100 % in the range 224 to 11.2 µg/tube. There was no sample degeneration during storage up to 14 day both under refrigerated and ambient conditions. It may be possible to analyze other amines at the same time.	Medium maturity: OSHA method PV2145. Partially validated. (OSHA PV2145)
air	DEA specific	Q	Sampling on glass tubes containing XAD-2 resin coated with 10 % (w/w) NITC. NITC works as derivatization agent forming a stable derivative. Extraction with dimethylformamide.	60 min at 0.05 l/min (3 l)	Overall 0.04 ppm based on 10 l air volume.	Target concentration 25 ppm (88 mg/m^3). Desorption efficiency from sampling tubes mean of 100 %. Sample storage: the recovery remained above 92.5 % for a 16 days storage period. Suggested confirmation method: GC/MS.	Medium maturity: OSHA method PV2018. Partially validated. (OSHA PV2018)
air	MEA specific	Q	Sampling on glass tubes containing XAD-2 resin coated with 10 % (w/w) NITC. NITC works as derivatization agent forming a stable derivative. Extraction with dimethylformamide.	0.1 l/min (10 l)	Overall 0.06 ppm based on 10 l air volume.	Target concentration 3 ppm (6 mg/m^3). Desorption efficiency from sampling tubes mean of 100 %. Sample storage: the recovery remained above 98.1 % for a 16 days storage period. Suggested confirmation method: GC/MS.	Medium maturity: OSHA method PV2111. Partially validated. (OSHA PV2111)

Matrix	**Compound**	**Method type**	**Adsorbent**	**Sampling rate**	**LOD**	**Characteristics**	**Maturity/Ref**
air	EDA, (DETA, TETA) specific (DETA=diethylenetriamine, TETA=triethylenetetramine)	Q	Sampling on glass tubes containing XAD-2 resin coated with 10 % (w/w) 1-naphthylisothiocyanate (NITC). NITC works as derivatization agent forming a stable derivative. Extraction with dimethylformamide.	0.1 l/min (10 l)	Overall and reliable quantitation limit: 0.37 mg/m^3, (0.15 ppm) for EDA.	Desorption efficiency from sampling tubes mean of 100 %. Sample storage: the recovery remained above 92 % (EDA) for a 15 days storage period. Precision of the overall procedure: 10.7 for EDA. The linearity of the method was studied.	High maturity: OSHA method 60. Fully validated. (OSHA 60)
air	MEA, DEA. Primary and secondary alkanolamines		Sampling on silica gel tubes, desorption with 4:1 MeOH:water under acidic conditions.		1 µg/tube.	DIPA (diisopropanolamine) was also present in the matrix. One of DIPA isomers did not completely resolve from MEA. Linearity range: 2-200 µg/ml. Desorption efficiency form silica gel tubes: MEA: 89-52.3 % DEA: 78.5-49.3 %. The recovery increased with the amount of alkanolamine in the sample. Good storage stability of the samples.	Low maturity: Article (Serbin & Birkholz 1995)

Matrix	**Compound**	**Method type**	**Adsorbent**	**Sampling rate**	**LOD**	**Characteristics**	**Maturity/Ref**
ambient air	MMA, DMA and alkanolamines **DEA** and **MEA**. Other primary and secondary low molecular weight amines	Q	Sampling with glass fiber cassettes treated with H_2SO_4 in MeOH. Elution and derivatization with dansyl chloride in acetonitrile and water (dansylation).	1 l/min for 15 min	Limit of quantification with external calibration(μg/ml): DEA 0.09, MEA 0.05, MMA 0.02, DMA 0.07	Sensitivity with external calibration (ml/μg): DEA $1.5{\cdot}10^7$, MEA $1.7{\cdot}10^7$, MMA $3.4{\cdot}10^7$, DMA $4.2{\cdot}10^7$ Recovery was close to 100 % for all the amines. LOQ and sensitivity for internal calibration are also given.	Low maturity: Article (Fournier et al. 2008)
air	MEA, DEA, (TEA, triethanolamine). Aminoethanol compounds.	Q	Sampling: impinger with hexanesulfonic acid.	0.5 to 1 l/min (vol. min 5 l, max 300 l)	MEA 7 DEA 13 µg/sample LOQ: MEA 20 DEA 40 µg/sample	Working ranges: MEA 0.08-12 ppm (0.2 – 30 mg/m^3) DEA 0.09-7 ppm (0.4 – 30 mg/m^3) for 100 l air sample. Interferences: larger amines do not interfere, LMW amines might. Na and NH_4^+ ions may interfere with MEA. Method evaluated for DEA.Recovery: 70-95 %. Stable at least 3 weeks at 20 °C (routine shipment)	Medium maturity: NIOSH method 3509. Partially evaluated. (NIOSH 1994d)

5.5.2 Evaluation of methods for solvent amine sampling

Evaluation of sampling methods is presented at Table 11.

Table 11 Different sampling approaches of solvent amine sampling

Method	Advantage	Disadvantage
XAD-2 (with NITC) and XAD-4 (with cyclohexanone)	May be suitable for the flue gas sampling. Good storage stability of the samples. (OSHA PV2060) XAD-4 suitable also for ammonia collection. (Gaind et al. 1992) There was no sample degeneration during storage up to 14 day both under refrigerated and ambient conditions (XAD-2) (OSHA PV2145). Multiple amine collection at the same time. Simultaneous derivatization.	May concentrate precursor amines and nitrosating agents resulting in artifactual in situ formation of the analyte. Known artifact formation.
Silica gel	Relatively selective (McDermott 2004). Good storage stability of the samples (Serbin & Birkholz 1995).	Silica gel may have a reduced capacity at high humidity (McDermott 2004).
Film chemisorption tubes in acid conditions		NH_3 and other amines that react with H_2SO_4 can decrease the chemisorption capacity of the tube (Zenkevich & Chupalov 1996).
Glass fiber cassette	Derivatization can be done during elution (Fournier et al. 2008). Good recovery, fast flow rate, could be suitable for high temperatures.	
Impinger	Good recovery. Stable at least 3 weeks at 20 °C (NIOSH 3509).	LMW amines might interfere (NIOSH 3509). Na and NH_4^+ ions may interfere with MEA.

Again, there is a lack of sampling of emission gas and the presented methods are for other air samples. According to OSHA, XAD-2 resins are extensively used in solvent amine sampling (OSHA PV2145, PV2018, PV2111, 60). NIOSH, instead of solid sorbents, presents an impinger with hexasulfonic acid for a sampling method. However, the method (either OSHA or NIOSH) suitability for intended emission gas sampling is not guaranteed and needs to be examined.

5.6 Amides - Sampling methods

Only few sampling methods were found for amides (Table 12). For example silica gel and Tenax TA have been used in sampling.

Table 12 Sampling methods for amides.

Matrix	Compound	Method type	Adsorbent	Sampling rate	LOD	Characteristics	Maturity/Ref
air	Acetamide specific	Q	Sampling with silica gel tube. Desorption with MeOH.	0.1 l/min (10 l)	10 ng/sample (0.4 ppm based on a 10 l sample).	It may be possible to analyze other compounds at the same time. Average desorption efficiency from the silica tubes: 94.4 %. Seven days storage test: 94.1 % average recovery.	Medium maturity: OSHA method 2084 (OSHA 2084). Partially Validated. Stopgap method.
dust particles in air	Acetamide, (ammonia). LMW compounds (VOC and inorganic) adsorbed onto dust particles.	Q	Sampling and pre-treatment for collection of dust particles and desorption of the chemical compounds from the dust particles (in a thermal desorption oven).				Low maturity: Article (Nilsson et al. 2002)
cigarette mainstream smoke	Acetamide (and acrylamide)	Q	Pre-treatment for cigarette mainstream smoke. Elution of the compounds from collection pads by means on acetone.		70 ng/ml	Linearity range: 0.338 – 32.2 µg/ml.	Low maturity: Article (Diekmann et al. 2008)
air	Formamide (VOC)	Q	Sampling of VOC with glass tubes packed with Tenax TA. Thermal desorption.	100 ml/min			Low maturity: Article (Karpe et al. 1995)
air	Acetamide. VOC	Q	Sampling (Tapered element oscillating microbalance (TEOM) filter) and pre-treatment for swine barn particulate. Analysis of VOC extracts.				Low maturity: Article (Cai et al. 2006)

Only few methods are presented for amide sampling. According to OSHA (OSHA 2084), silica gel might be a proper sampling material for amides. Also other solid sorbents, such as Tenax, might be suitable (Karpe et al. 1995). It seems that sampling of the different compound groups is needed to be performed with distinct manners.

5.7 Aldehydes

For aldehydes (acetaldehyde and formaldehyde), many adsorbents have been used (Table 13). In the methods by NIOSH and OSHA the sample is collected to XAD-2 sorbent tubes (2-HMP on XAD-2, 120 mg / 60 mg), where 2-HMP is the derivatization agent. Also widely used method is the cartridges containing silica gel coated with 2,4-dinitrophenylhydrazine (2,4-DNPH, derivatization agent). Among others, DNPH method has been employed in NILU, NIOSH, OSHA and EPA standard methods. In addition, Girard T solution and impinger samplers have been used.

5.7.1 Sampling methods for aldehydes

Table 13 Sampling methods for aldehydes

Matrix	Compound	Method type	Adsorbent	Sampling rate	LOD	Characteristics	Maturity/Ref
air, bulk field samples	Acetaldehyde, formaldehyde.	S	Sampling and derivatization on sorbent tubes (2-HMP on XAD-2, 120 mg / 60 mg). 2-HMP is the derivatization agent. Desorption with toluene.	0.01 to 0.05 l/min (5 l)	Estimated 2 µg aldehyde per sample.	Shipment at 25 °C or lower. Sample stability at least 1 week at 25 °C	Medium maturity: NIOSH method 2539. Partially validated. (NIOSH 1994d)
air	Acetaldehyde specific	Q	Sampling and derivatization on sorbent tubes (2-HMP on XAD-2, 120 mg / 60 mg). 2-HMP is the derivatization agent. Desorption with toluene.	0.01 to 0.05 l/min (vol. min 1 l at 100 ppm, max 12 l)	Estimated 2 µg per sample.	Working range: 0.74 – 407 ppm (1.3 – 730 mg/m^3) for a 3 l air sample. Recovery was 100% after 21 days when stored at 0 °C. Routine shipment.	Medium maturity: NIOSH method 2538. Evaluation: unrated. Modification of OSHA method 68 (NIOSH 1994a, OSHA)
air	Acetaldehyde specific	Q	Sampling and derivatization on sorbent tubes (2-HMP on XAD-2, 120 mg / 60 mg). 2-HMP is the derivatization agent. Desorption with toluene.	0.05 l/min (3 l)	Reliable LOQ (and LOD): 1050 µg/m^3.	The recovery of acetaldehyde stored for 23 days at room temperature was above 92.8 %. Interferences: mineral acids may neutralize 2-HMP. Chemical which contain a carbonyl group (such as acetone) may react with 2-HMP. The response was not linear in the range of 0.5 to 2 times the target concentration (200 ppm, 360mg/m^3).	High maturity: OSHA method 68. (OSHA 68) Fully validated.

Matrix	Compound	Method type	Adsorbent	Sampling rate	LOD	Characteristics	Maturity/Ref
air	Formaldehyde (and Acrolein)	Q	Sampling and derivatization on sorbent tubes (2-HMP on XAD-2, 120 mg / 60 mg). 2-HMP is the derivatization agent. Desorption with toluene.	0.1 l/min (24 l)	Reliable LOQ (formaldehyde): 16 ppb (20 µg/m^3)	The recovery of formaldehyde form samples over an 18 days storage test remained above 92 %. The average desorption efficiency of formaldehyde from the sampling device was 96.2 %.	High maturity: OSHA method 52. (OSHA 52) Fully validated.
air	Formaldehyde (and acrolein)	Q	Sampling and derivatization on sorbent tubes (2-HMP on XAD-2, 120 mg / 60 mg). 2-HMP is the derivatization agent. Desorption with toluene.	0.01 to 0.10 l/min (Vol. 1 – 36 l at 3 ppm)	Estimated 1 µg/sample	Working range: 0.24 – 16 ppm (0.3 – 20 mg/m^3) for a 10 l air sample. Acid mist may inactivate the sorbent leading to inefficient collection of formaldehyde. Sample stability 3 weeks at 25 °C, routine shipment.	Medium maturity: NIOSH method 2541. Partially Validated. (NIOSH 1994e)
air	Formaldehyde, acetaldehyde and other carbonyl compounds	Q	Sampling and derivatization onto 2,3,4,5,6-pentafluorophenyl hydrazine (PFPH) coated Tenax solid sorbents. PFPH is the derivatization agent. Thermal desorption (TD). Ozone trap. Comparison with DNPH cartridge.	100 ml/min, time 15 min to 4 h	0.26 ppbv with an air sample volume of 24 l for formaldehyde and 0.1 ppbv for acetaldehyde	Linearity range: 0.5- 2.5 nmol/tube (r^2> 0.991). The LOD of the DNPH-EPA method (EPA 1999): 0.58 ppbv for both. The collection efficiency of the DNPH-EPA cartridges was > 95% (flow rate 2 l/min). The efficiency > 91% at the lowest flow rate (54 ml/min). The efficiency decreased with increasing flow rate.	Low maturity: Article (Ho & Yu 2004) A similar method is also proposed by (Li et al. 2009)
cigarette smoke	Aliphatic and aromatic aldehydes	Q	Derivatization with cysteamine into thiazolidine derivatives.		4-100 pg injected	Linearity range: 20 – 2500 ng.	Low maturity: Article (Kataoka et al. 1997)

Matrix	Compound	Method type	Adsorbent	Sampling rate	LOD	Characteristics	Maturity/Ref
air	Formaldehyde, acetaldehyde (and other aldehydes and ketones)	Q	Sampling with an air sampler pump with impingers. Derivatization with 4-dimethylamino-6-(4-methoxy-1-naphtyl)-1,3,5-triazine-2-hydrazine (DMNTH).	1.25 l/min (10 l)	formaldehyde $5\cdot10^{-8}$ mol/l, acetaldehyde $2\cdot10^{-8}$	Linearity was observed up to $5\cdot10^{-5}$ mol/l.	Low maturity: Article (Kempter et al. 1999)
air	Formaldehyde, acetaldehyde (and other aldehydes and ketones)	Q	Sampling and derivatization with 2,4-dinitrophenylhydrazine (DNPH) on DNPH coated silica gel cartridges. Elution with acetonitrile.	1 l/min (3 or 4 l)	*APPI mode:* LOD: formaldehyde $24\cdot10^{-9}$ M, acetaldehyde $8.8\cdot10^{-9}$ M LOQ: formaldehyde $80\cdot10^{-9}$ M, acetaldehyde $29\cdot10^{-9}$ M, *APCI mode:* LOD: formaldehyde $70\cdot10^{-9}$ M, acetaldehyde $73\cdot10^{-9}$ M, LOQ: formaldehyde $234\cdot10^{-9}$ M, acetaldehyde $244\cdot10^{-9}$ M	Linearity: r2>0.986 for APPI mode, r2>0.996 for APCI mode.	Low maturity: Article (Van Leeuwen et al. 2004)

Matrix	**Compound**	**Method type**	**Adsorbent**	**Sampling rate**	**LOD**	**Characteristics**	**Maturity/Ref**
ambient air	Aldehydes and ketones		Sampling and derivatization on a cartridge containing DNPH-coated silica packed in a polyethylene tube. (Sep-PAK DNPH-silica cartridges). The sampling equipment is equipped with an ozone scrubber using potassium iodide. Elution with Acetonitrile.		For typical sample (750 l): 0.01 – 0.05 µg/m^3	Range of use: 0.1 – 10 µg/m^3.	Medium to high maturity: EMEP method. (NILU. Norwegian Institute for Air Research. 2001) A structure analysis of the DNPH derivatives is performed in (Koelliker et al. 1998) by means of **HPLC-MS** and **HPLC-MS/MS**
air	Acetaldehyde specific	Q	Sampling and derivatization in midget bubbler containing 15 ml Girard T solution (pH 4.5). Girard T reagent [(carboxymethyl)-trimethylammonium chloride hydrazine recrystallised from 95 % ethanol] is the derivatization agent.	0.1 to 0.5 l/min (6-60 l at 200 ppm)	0.1 mg per sample	Working range: 18 – 372 ppm (33 – 670 mg/m^3) for a 60 l air sample. **NB**: Interferences: other volatile aldehydes and ketones (e.g. acetone, acrolein and **formaldehyde**) compete for the Girard T reagent, which should be kept at a two-fold molar excess over aldehyde concentration. GC conditions might be adjusted to resolve acetaldehyde from other aldehydes. Girard T solution must be used within 2 weeks. Sample stability 1 week in 25 °C at dark.	High maturity: NIOSH method 3507 (NIOSH 1994b). Fully validated

Matrix	Compound	Method type	Adsorbent	Sampling rate	LOD	Characteristics	Maturity/Ref
air	Formaldehyde specific	Q	Sampling and derivatization on cartridges containing silica gel and coated with DNPH, a derivatization agent. Elution with carbonyl-free acetonitrile. Acetonitrile should be checked for formaldehyde content by elution and analysis of a blank cartridge and it should be below the detection limits.	0.03 to 1.5 l/min (vol. min 1 l at 0.25 mg/m^3, max 15 l at 2.5 mg/m^3)	Estimated 0.07 µg/sample	Working range: 0.015 – 2.5 mg/m^3 (0.012 – 2.0 ppm) for a 15 l sample. Ozone consumes 2,4-DNPH and degrades the formaldehyde derivatives. Ketones and other aldehydes can react with 2,4-DNPH but the derivatives produced are separated chromatographically from the formaldehyde derivative. Sample stability 34 days at 5 °C. Shipment on ice.	High maturity: NIOSH method 2016 (NIOSH 1994g). Fully validated
air	Formaldehyde specific	Q	Sampling and derivatization with Supleco DSD-DNPH Diffusing Sampling Device. (Two other sampling devices were tested, with worse performances in terms of LRQ). DNPH in presence of a strong acid is the derivatization agent. Formaldehyde gives a unique derivative. Elution with acetonitrile.		Reliable quantitation limit (LRQ): 0.58 ppb (0.7 µg/m^3). LOD: 0.17 ppb (0.21 µg/m^3).	These diffusive samplers should not be used if the ozone level is greater than 0.5 ppm or the humidity 10% or less. The recovery of formaldehyde from samples in an 18-days storage test remained above 95.8 %. The mean extraction efficiency for formaldehyde was 100 % and it was not affected by the presence of water.	High maturity: OSHA method 1007 (OSHA 1007). Fully validated.

Matrix	**Compound**	**Method type**	**Adsorbent**	**Sampling rate**	**LOD**	**Characteristics**	**Maturity/Ref**
air	Formaldehyde (acetaldehyde and other carbonyl compounds)	Q	Sampling and derivatization with a pre-packed cartridge coated with acidified DNPH. Elution with acetonitrile.	100 – 1500 ml/min (air volume 50 – 100 l)	A procedure to calculate the LOD is given. LOD depends on the instruments and conditions used	Ozone consumes DNPH and degrades the formaldehyde derivatives. The most direct solution to this problem is to remove the ozone before the sample stream reaches the coated cartridge by means of a scrubber or denuder. The method was evaluated by round Robin test in the US, Canada and Europe.	High maturity: EPA method TO-11A (EPA 1999)
stack gas samples	Acetaldehyde, formaldehyde (and other carbonyl compounds)	Q	Gas (and particulates) are withdrawn isokinetically and collected in aqueous acidic DNPH (derivatization). Extraction with methylene chloride (LLE). The procedure for indoor air samples is slightly different.			Acetone and MeOH react with DNPH, therefore glassware should not be rinsed with these solvents. Formaldehyde contamination of DNPH is often encountered.	High maturity: US EPA method 8315A. Procedure 2. Sampling: US EPA method 0011. (EPA 1996b, EPA 1996a)
air	Formaldehyde, acetaldehyde (and other carbonyl compounds)	Q	Sampling and derivatization with Sep-Pak Silica Gel cartridge coated with a solution of DNPH and acetonitrile (with *ortho*-phosphoric acid). A potassium iodide denuder was used during sampling to prevent ozone interferences. Elution with acetonitrile.		Formaldehyde 1.9 ng/m^3, acetaldehyde 5.2 ng/m^3	Ozone consumes DNPH and degrades the derivatives. A potassium iodide denuder was used to prevent ozone interferences. Mean recovery %: Formaldehyde 100, acetaldehyde 92 Linearity range: 10 – 450 µg/l ($r^2>0.9938$).	Low maturity: Article (Chi et al. 2007)

Matrix	**Compound**	**Method type**	**Adsorbent**	**Sampling rate**	**LOD**	**Characteristics**	**Maturity/Ref**
air	Formaldehyde, acetaldehyde (and other aldehydes)	Q	Sampling and derivatization on octadecysilica modified cartridges with dansylhydrazine (DNSH) in presence of trichloroacetic acid. Elution with MeOH.	1.0 l/min (2h 15 min)	LOD (CE-UV): formaldehyde 1.1 µg/l, acetaldehyde 7.6 µg/l, LOQ (CE-UV): formaldehyde 3.6 µg/l, acetaldehyde 25 µg/l LOD (CE-LIF): formaldehyde 0.29 µg/l, acetaldehyde 3.2 µg/l LOQ (CE-LIF): formaldehyde 0.98 µg/l, acetaldehyde 11 µg/l		Low maturity: Article (Pereira et al. 2002)
air	Formaldehyde, acetaldehyde (and other aldehydes)	Q	Sampling and derivatization on octadecysilica modified cartridges with 4-hydrazinobenzoic acid (HBA) as derivatization agent. Elution with acetonitrile and water.	1.1 l/min (2 h, dark)	formaldehyde 2.7 ng/ml, acetaldehyde 4.6 ng/ml	The full separation of 4 aldehydes took less than 6 minutes. Linearity range: 50 – 300 µg/l with r^2> 0.998.	Low maturity: Article (Pereira et al. 2004)

Matrix	Compound	Method type	Adsorbent	Sampling rate	LOD	Characteristics	Maturity/Ref
air	Formaldehyde specific	Q	Sampling with filter + impingers (1 µm PTFE membrane and 2 impinger, each with 20 ml 1 % sodium bisulfite solution).	0.2 - 1 l/min (1-100 l at 3 ppm	Estimated 0.5 µg/sample	Working range: 0.02 – 4 ppm (0.025 – 4.6 mg/m3) for an 80 l air sample. Interferences: oxidizable organic materials may give a positive interference. Phenol to formaldehyde rations as low as 0.3 produce a -15 % bias. Ethanol and higher MW alcohols, olefins, aromatic hydrocarbons and cycloexanone also produce small negative interferences. Little interference is seen from other aldehydes. The calibration graph becomes non linear above an absorbance of ca. 1.0 A.U. Sample stability 30 days at 25 °C.	High maturity: NIOSH method 3500 (NIOSH 1994f). Fully validated

5.7.2 Evaluation of methods for acetaldehyde and formaldehyde sampling

Evaluation of sampling methods is presented at Table 14.

Table 14 Different sampling approaches of aldehyde sampling

Method	Advantage	Disadvantage
XAD-2 sorbent tube (10 % 2-(hydroxymethyl) piperidine (2-HMP) on XAD-2, 120 mg/ 60 mg)	May be suitable for the flue gas sampling. Good storage stability of the samples (NIOSH methods, Table 13). Simultaneous derivatization with 2-HMP.	Mineral acids may neutralize 2-HMP. Chemical which contain a carbonyl group (such as acetone) may react with 2-HMP (NIOSH methods, Table 13).
DNPH coated Silica Gel (e.g. Supelco DSD-DNPH and DNPH-EPA cartridges)	Good collection efficiency. Simultaneous derivatization. The recovery of formaldehyde after 18-days storage remained above 95.8 %. The mean extraction efficiency for formaldehyde was 100 % and it was not affected by the presence of water (OSHA method 52.).	Collection efficiency decreased with increasing flow rate (DNPH-EPA method). Ozone consumes DNPH and degrades the derivatives(NIOSH 2016). Supelco DSD-DNPH diffusive samplers should not be used if the ozone level is greater than 0.5 ppm or the humidity 10% or less (OSHA 1007).
Aqueous acidic DNPH	Simultaneous derivatization.	Ozone consumes DNPH and degrades the derivatives (NIOSH 2016). Might not be suitable for the field use.
Impinger with DMNTH	Simultaneous derivatization.	
Sampling with filter + impingers (1 µm PTFE membrane and 2 impinger, each with 20 ml 1 % sodium bisulfite solution)		Oxidizable organic materials may give a positive interference (NIOSH 3500).
Silica gel with HBA	Simultaneous derivatization.	
Octadecysilica modified cartridges with dansylhydrazine (DNSH) in presence of trichloroacetic acid.	Simultaneous derivatization.	
PFPH coated Tenax solid sorbents	Simultaneous derivatization.	
Girard T	Simultaneous derivatization.	Other volatile aldehydes and ketones compete for the Girard T reagent, which should be kept at a two-fold molar excess over aldehyde concentration. Girard T solution must be used within 2 weeks (NIOSH 3507).

According to literature survey, DNPH coated silica and XAD-2 resin are the most used sampling materials. Multiple standard methods suggest these solid sorbents to be used (Table 13), but the sampling have been performed in basic air samples. Since XAD-2 was suitable for aldehyde sampling as well, these two compound groups might be able to be sampled at once.

5.8 Ammonia - Sampling methods

For ammonia sampling, sulphuric acid (on solid sorbent or as liquid) has been used. The OSHA, EPA and NIOSH among couple of other methods are presented at Table 15.

Table 15 Sampling methods for ammonia.

Matrix	Adsorbent	Sampling rate	LOD	Characteristics	Maturity/Ref
Flue gas (coal fired boiler)	Four impingers in a row with 0,1 N H_2SO_4	liters/minute (isokinetic)			Medium maturity: EPA Draft Conditional test method CTM-027
air, workplace atmosphere	A known volume of air is drawn through a glass midget bubbler containing approximately 10 mL of 0.1 N H_2SO_4	1 l/min	2.0 µg NH_3 in solution	Recommended air volume 120 l	Medium maturity: OSHA method 164, partially validated (OSHA 164)
air, workplace atmosphere	A personal sampling pump is used to draw a known volume of air through a glass tube containing carbon beads impregnated with sulfuric acid (CISA). The sample is desorbed with deionized water and analyzed as ammonium ion using an IC.	l/min (TWA determination), 0.5 l/min (STEL determination) (TWA= time-weighted average, STEL= short-term exposure limits)	0.60 ppm (24-l air sample) 1.9 ppm (7.5-L.air sample)	Recommended air volume 24 l for TWA and 7.5 l for STEL. Validation range 30.7 to 101.8 ppm	Medium maturity: OSHA method 188, validated (OSHA 188)
air	Solid sorbent tube (sulfuric acid-treated silica gel) A 0.8-micron MCE prefilter may be used to remove particulate interferences.	0.1 to 0.2 l/min	0.5 µg per sample, air volume 0.1 – 60 l at 50 ppm	The working range is 0.2 to 400 ppm (0.15 to 300 mg/m 3) for a 10-L air sample. This method is applicable to STEL measurements. Routine shipment.	Medium maturity: NIOSH 6015 (NIOSH 1994h)
air	Solid sorbent tube (sulfuric acid-treated silica gel) a 0.8-µm MCE prefilter may be used to remove particulate interferences.	0.1 to 0.5 l/min	2 µg per sample	The working range is 24 to 98 ppm (17 to 68 mg/m^3) for a 30-l sample. This method is applicable to STEL measurements when sampled at 0.2 l/min.	Medium maturity: NIOSH 6016 (NIOSH 1996)
dust particles in air (Ammonia among acetamide)	Sampling and pre-treatment for collection of dust particles and desorption of the chemical compounds from the dust particles (in a thermal desorption oven).				Low maturity: Article (Nilsson et al. 2002)
ambient air (Ammonia among MEA and other aliphatic amines)	XAD-4 resin coated with cyclohexanone as derivatization agent. Desorption with MeOH.	0.2 l/min (20 l)	1µg	Relative humidity 45%. Stable derivatives: collected samples were stable ≥ 2 weeks.	Low maturity: Article (Gaind et al. 1992)

For ammonia sampling sulphuric acid (liquid or treated carbon/silica gel) might be the method of choice according to OSHA (method 164 and 188), NIOSH (6015 and 6016) and EPA CTM 027. For all sulphuric acid based methods analysis are disturbed by amines and the analysis result is sum of amines and ammonia.
Derivatization based methods should be developed during the subtask 5.

6. SAMPLING SYSTEM FOR AMINES AND AMIDES

6.1 Basic principle of sampling system

The basic principles of the design of manual sampling system are:

1. Acquire representative sample
2. Avoid reactive materials and conditions
3. Minimize the contact between the sample and flue gas during sampling
4. Maximize a number of different analytes to sample at once
5. Keep the sampling system as simple as possible to avoid potential error sources

Gas should be taken as isokinetic sampling if water drops or droplets are assumed to be present in flue gas. Whilst in some studies it is presented that very small droplet behave like gas and isokinetic sampling is not necessary (Zhu, 1999), some other practical studies shows wider divergence between parallel samples taken as un-isokinetic (EN 1948-1). Also size of the droplets is not assured for example at the case of accidental emission.

Because some of the amines may decompose by heat, water or oxidation, heated parts on sampling system are not recommended with exception of very cold weather conditions to avoid freezing. In practice this means that filtration or sampling with the side stream (as used in some isokinetic sampling installations) before condensation is not in practice possible, because division of sample gas for separate homogeneous flows is difficult if liquid water is present.

It is presumable that flue gas may affect the samples acquired within sampling time. To reduce possible artefact formation or degradation, contact between the flue gas and condensed water should be minimized. One approach is to obtain “dry impinger method”. All materials contact with flue gas has to be inert against the amines. This covers also absorbents. Dry impinger method is applied from EPA OTM 28, *Dry impinger method for determining condensable particulate emissions from stationary sources.* Also typical practices and approaches presented on the PCDD/F and HCl sampling are applied (EN standards 1948-1 and 1911:2010).

The system is designed to allow division of “dry” sample flow to the different absorption systems. Also higher flow rates through the nozzle needed for the isokinetic sampling is possible along with relatively slower sampling rates onto absorbents.

6.2 Sampling equipment

Sampling equipment consists of six parts:

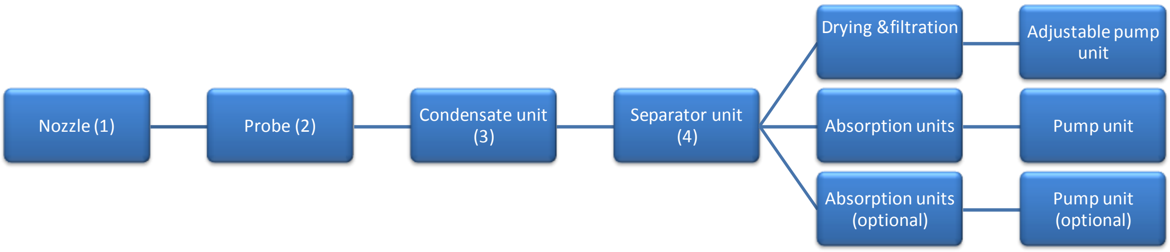

Figure 1. Basic principle of proposed sampling arrangement

Part	Purpose
1. Nozzle	Known design and size allows isokinetic sampling at adequate flow rate.
2. Probe	Achieve a representative sampling from different points of a duct area without decomposition. Pre-cool the sample.
3. Condensate unit	Condense condensable compounds and droplets into liquid phase. Lowers the humidity to equate the dew point of cooler temperature.
4. Separation unit	Divide the sample gas into separate homogeneous concentrations and sampling trains to allow parallel sampling trains and adjustment of isokinetic sampling
5. absorption units	Collect compounds into different mediums
6. pump units	Sample gas drying and measuring (temp, amount). Flow rate adjustment.

Cooled probe is suitable for the conditions where the dust concentration is expected to be at low level and flue gas is humid. The acquired sample is combination of gas, liquid and solid phase of flue gas. Distinction between the solid and gaseous phase cannot be done.

Cooled probe does not allow filtering before condensation. Filtering of CCS-plant exhaust gas on manual sampling is not recommended because of heat needed on the filtering. Some of the compounds are thermally labile (e.g. MEA) at elevated temperatures and flue gas containing oxygen and water. Filter needs to be heated at least 10-20 °C over the dew point to avoid condensation onto filter. If a heated filter is used, it should take into account that salts normally dissolved in water will condensate on filter.

On presented method sample gas is possible to separate after cooling and condensation. This is not necessary if all needed components could be analysed from the condensate liquid and one absorption line. Side stream with adjustable pump unit may be necessary to avoid over-bubbling from the impingers while taking samples at isokinetic conditions.

The proposed method is described more detailed at below.

6.2.1 Nozzle

The shape of the nozzle tip should be congruent with EN 13284-1 (European Committee For Standardization) (Figure 2.) to establish undisturbed isokinetic sampling conditions.

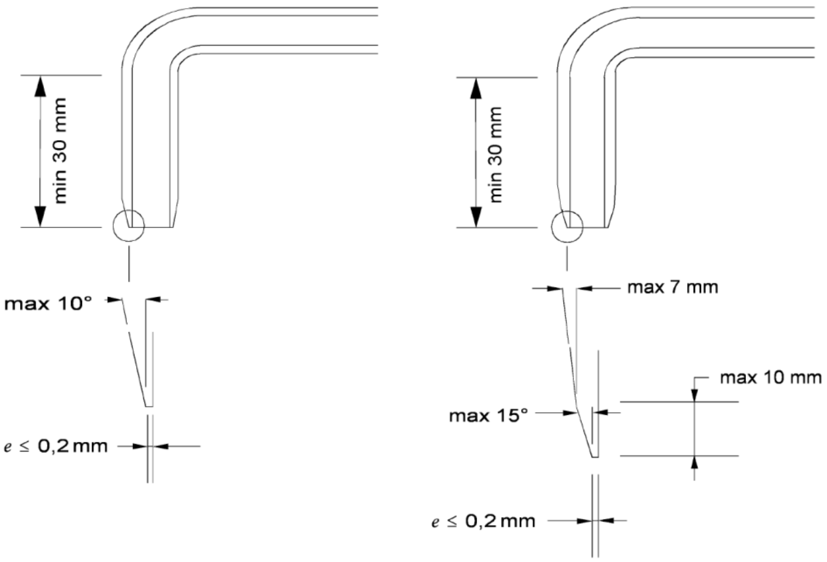

Figure 2. Recommended design of sampling nozzle

Recommended material for the nozzle tip is Stainless steel (304 SS, 304L SS, 316 SS and 316l SS are recommended for general use). However, quartz- or borosilicate glasses are also suitable but not recommended for the practical reasons. Usability of titanium alloys in sampling system is unclear (it is resistant against most of the compounds included in flue gas). Report of galvanically induced hydrogen embirttlement corrosion with rich MEA based processes at elevated temperatures (120 °C) is presented (McMaster & Rowan 2000).

Nozzle size should allow isokinetic sampling in flow rates 5- 20 m/s. Typical nozzle diameters at the different flow and sampling rates (sampling rate presented on flue gas conditions) are presented at Table 16. The maximum sampling rate is limited by the maximum sampling rate through absorption cartridge or impinger vessel.

Table 16 Typical (green) nozzle diameter at different flow and sampling rates (sampling rate presented on flue gas conditions

Nozzle size (diameter, mm)											
	sampling rate (l/min)										
Flow rate (m/s)	**0,2**	**0,5**	**1**	**2**	**4**	**6**	**8**	**10**	**12**	**16**	**20**
2	1,5	2,3	3,3	4,6	6,5	8,0	9,2	10,3	11,3	13,0	14,6
4	1,0	1,6	2,3	3,3	4,6	5,6	6,5	7,3	8,0	9,2	10,3
6	0,8	1,3	1,9	2,7	3,8	4,6	5,3	5,9	6,5	7,5	8,4
8	0,7	1,2	1,6	2,3	3,3	4,0	4,6	5,2	5,6	6,5	7,3
10	0,7	1,0	1,5	2,1	2,9	3,6	4,1	4,6	5,0	5,8	6,5
12	0,6	0,9	1,3	1,9	2,7	3,3	3,8	4,2	4,6	5,3	5,9
14	0,6	0,9	1,2	1,7	2,5	3,0	3,5	3,9	4,3	4,9	5,5
16	0,5	0,8	1,2	1,6	2,3	2,8	3,3	3,6	4,0	4,6	5,2
18	0,5	0,8	1,1	1,5	2,2	2,7	3,1	3,4	3,8	4,3	4,9
20	0,5	0,7	1,0	1,5	2,1	2,5	2,9	3,3	3,6	4,1	4,6

On low sampling rates (< 1 l/min) and typical flow rates (10-15 m/s) the needed nozzle size is quite small for the isokinetic sampling, see Table 16. This may be notice when selecting the type of absorbers. Otherwise adjustable side stream shall be used to obtain adequate sample flow.

6.2.2 Probe

The probe should be about 0.5-1 meter longer than the diameter of duct. If two opposed sampling ports are available half of the duct diameter + 0.5- 1 m is adequate for the sampling probe.

Recommended liner material is stainless steel (e.g. SS316) or glass. At the temperatures near or above 100 °C sampling probe should be cooled on water to avoid drying inside the sample tube. One benefit on cool probe system is "auto cleaning" of the probe tubing from dust, salts and SVOC etc. by condensing water. This reduces possible side-reactions in the probe along with lower temperature compared to heated probe.

Recommended temperature of the probe is below the flue gas temperature measured at the coolest part of the probe to ensure proper condensation at condensate unit. If hot gas is measured at high velocities (~ 200 °C) liner should be cooled by water.

Flue gas velocity shall be measured from any traverse point using S-type Pitot-tube. Pitot-tube shall be attached to the sampling probe (if combined probe is not available) to allow constant monitoring of the stack gas velocity. The impact (high pressure) opening plane of the Pitot-tube shall be even with or above the nozzle entry plane during sampling.

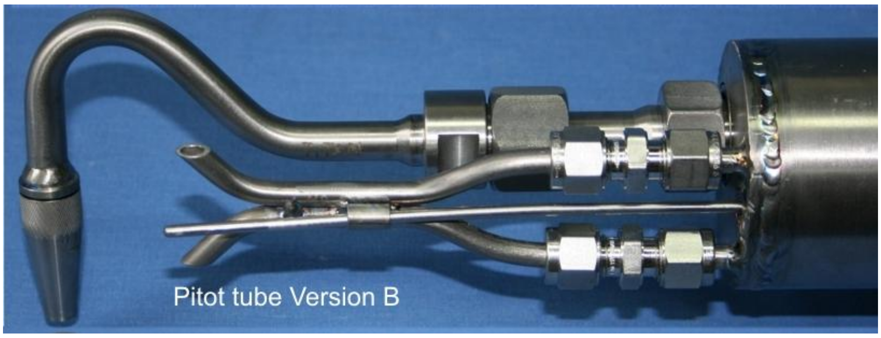

Figure 3. Probe head with pitot tube and thermal element, Paul Gothe Messtechnik

6.2.3 Condenser and condensate unit

Spiral condenser is recommended to allow sufficient cooling of flue gas. For this purpose a vertical spiral glass or SS cooler is recommended. Glass cooler is recommended to allow easier observation of possible blocking and while cleaning the parts after sampling. Cooling water temperature in the spiral should be as low as possible, however freezing should be avoided. Typical height of the condenser is about 300 mm.

At the case of water soluble or miscible compounds (like amines) significant amount of analyte is expected to retain in condensate. At some applications it may be necessary to insert preservation chemical in the dropout vessel before the sampling. However this should be carefully evaluated to avoid unwanted side reactions.

Dropout vessel should be designed to avoid percolation through the condensate liquid. Also contact between the sample gas and condensed water should be minimized. This could be done by using modified Greenburg-Smith impinger with the short stem, see Figure 4. Dropout vessel should be dry at the beginning of the sampling.

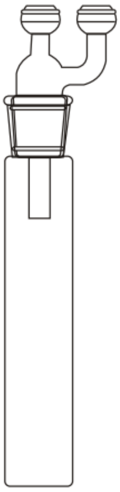

Figure 4. Modified Greenburg-Smith impinger with th short stem

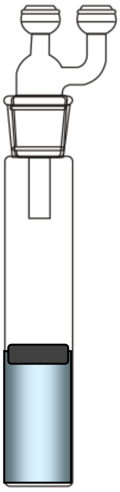

Figure 5. Modified Greenburg-Smith impinger with the float

To minimize contact between the condensate and flue gas an inert material float could be installed in the impinger, see Figure 5. The diameter of the float needs to be smaller than the diameter of the impinger to allow water to flow at the bottom of the impinger. Roughly 1 m^3 of flue gas containing 3 %-v of water yields 24 ml water. Thus 250 ml volume of dropout flask is adequate for the most purposes.

On solution to minimize contact between the flue gas and condensate is to use cyclone body and flask, Figure 6.

Figure 6. The principle of the cyclone type of body and flask

Condenser flask or impinger shall be placed at water bath, temperature < 20 °C; ice bath is preferred.

6.2.4 Separation unit

The separation unit divides droplet-free sample gas into the separate flows. This allows parallel sampling onto different absorbents (if needed) and adjustment of overall sampling rate to obtain isokinetic condition at the nozzle. If breakthrough of the droplets is present after condensate unit, sample gas should be heated to the stack temperature (maximum) before separation. Other solution is to use aerosol filter before separation unit, but this is not recommended. If aerosol filter is used it is part of the sample and needs to be inert material.

Material of the separation unit may be glass, but in practice SS with relatively small dimension is more flexible, rugged and easily slightly heated (at stack temperature maximum) if needed to avoid possible post-condensation.

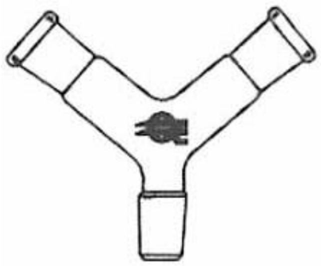

Figure 7.Example of the Y-piece used at separation

6.2.5 Absorption unit

Absorption unit may consist of either impingers, solid absorbent cartridges or both. Absorption matrix is selected according to target compounds.

According to literature survey standard methods for the CCS-plant flue gas sampling is not available. The absorption methods used on industrial hygiene sampling are not necessarily adequate, because the matrix of flue gas is significantly different.

The absorption methods below are presented as a start point of designing sampling system of CCS-plant flue gas. These practices will specify during the subtask 5.

Because detailed information and concentration of the amine based CCS-plant flue gas is not available, the approach is to use as simple sampling arrangement as possible. Principle is not to disturb the sample, so the absorption chemicals are not recommended at the start point of the method development for water soluble amines. Because nitrosamines, alkylamines and solvent amines are soluble in water the recommended absorption medium is contaminant free, pure water. Amides are also well soluble in water (e.g. formamide 1000 g/l).

Ammonia, acetaldehyde and formaldehyde also dissolve into water. Even there are some methods commonly used for sampling the mentioned compounds, those are not validated to amine rich flue gas and some interference are expected as described below.

Absorption units are installed after the condensate unit (if one sampling train is on use) or after the separation unit. It shall consist of at least four consecutive Greenburg-Smith impinger vessels with the long stem. Sintered frit is recommended at the end of the stem. Water level in the impinger vessels should be at least 40 mm over the sinter top at the beginning of the sampling.

It may be possible to sample ammonia at the same arrangement since ammonia is very soluble into water (898 g/l @ 0 °C). Also aldehydes are very soluble into water. However, possibility for side reactions and absorption efficiency at real samples should be evaluated.

6.2.6 Aerosol filter (optional)

If during validation appears that condensing units do not remove all of the moisture at aerosol size, aerosols may be present after the impingers. In that case aerosols must be filtered to avoid compounds to run-off. Suitable material for the filters is quartz.

NOTE 1: Filter efficiency better than 99.5 % on a test aerosol with a mean particle diameter of 0.3 m, at the maximum flow rate anticipated (or 99.9 % an a test aerosol of 0.6 µm mean diameter). This is fulfilled by the filters approved for EN 13284-1 sampling.

NOTE 2: Aerosol filter is part of the sample and preservation and analysis should be extended onto it.

NOTE 3: Quartz filters may be cause formation of degradation products on nitrosamines if preservation chemical is not used.

6.2.7 Solid absorbent (optional)

If during analysis and sampling method development it appears that impingers are not sufficient to trap all the selected compounds a solid sorbent must be used. The solid absorbent should include an aerosol filter or if not possible, mounted after the one. Absorption material and sampler design is described more detailed at the report of Subtask 5.

6.2.8 Pumping and measuring devices

Sample gas should be dried by automated drying system or using silica gel (or suchlike) before the suction pump. It is a good practise to install an empty and clean impinger before the silica gel to avoid sample flow into the silica gel at the case of possible over flow of absorbent liquid.

Pump should be adjustable i.e. bypass valve between in and out connection of the pump or recommended or electric inverter adjustment are recommended. If suction unit is used on ATEX-areas it should fulfil the requirements at the area or it should be moved to the safe area by using long sampling line. Significant head loss should be avoided. Pump inlet and outlet flows should be equal for making a flow measurement possible.

Accuracy of the volume measurement device shall not exceed ±2 %. Temperature of the volume measurement device should be observed and documented during the sampling.

Flow meter (e.g. rotameter) is recommended before the gas meter to allow faster observation and adjustment of flow rate during the sampling.

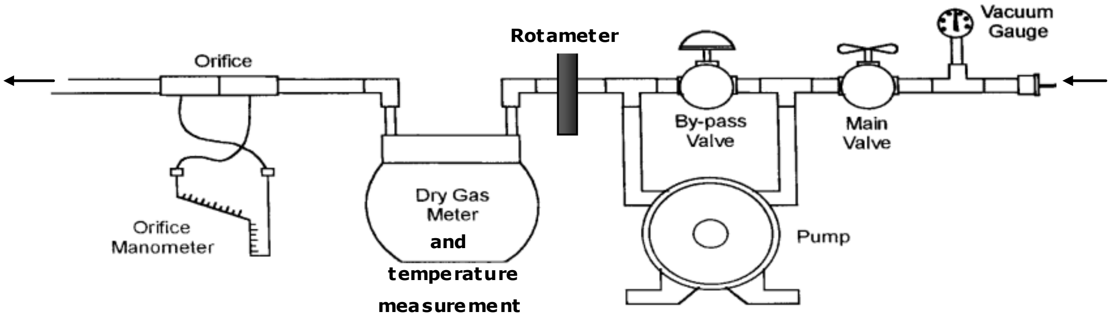

Figure 8. The design of the pumping and measuring devices

For isokinetic sampling, overall sampling rate measured at the nozzle should be possible to be obtained at 25 l/min. This depends on the speed of flue gas. Because in practice impingers do not allow sampling rates over 3-4 l/min the side flow sampling arrangement is needed when flue gas velocity exceeds 5-7 m/s. At these conditions two pump units or one pump with two gas meters (sampling and adjustment/overall) with separate flows are needed.

Automatic isokinetic control units are available by different vendors. The systems include pumps, flow meters, drying units and gas meters (Figure 9 and Figure 10).

Figure 9. Automatic isokinetic sampler (Paul Gothe)

Figure 10. Two orifices allows (Paul Gothe) use of side flow during the sampling

6.2.9 Materials

All materials on the sampling train shall resist corrosion of amines and ammonia. Glass and stainless steel (e.g. 304 SS, 304L SS, 316 SS and 316l SS) should be used. Ammonia, some amines and imines are reported to attack with PTFE (Ebnesajjad 2000). Even in presumably dilute solutions it should be evaluated if PTFE needs to be used. Other plastics are not recommended without evalution due to their reactions and absorption with amines.

6.2.10 Pros/cons of proposed sampling method

Table 17 Pros/cons of proposed sampling method

+	Sample is not disturbed (no evaporation, heating or filtration) before absorption
+	Low temperatures reduces possible artefact formation
+	Humidity can be measured at the same time
+	possibility to use parallel and different sample cartridges after the one condensing unit
+	Sampling is relatively easy to be performed
+	Loss of particles is minor due the self cleaning of water condensation
-	Maximum sampling rate may be limited on some absorbents
-	High concentration of dust or plugging by dust may cause problems due to sampling
-	Discrimination between solid and gas phase analysis is not possible
-	Unfiltered solids may cause transformation on sampling
-	At many cases sample needs to be at least extracted before sampling
-	Sample probe and lines needs to be cleaned or changed between separate samplings (contamination)
-	Freezing at very cold climates
-	Water cooling system may be needed

Table 18 presents differences between the heated probe sampling and recommended system. Heated probe system includes heated probe out-stack filter from where the sample gas flow is divided to adjustable pump and sample train flows. End of the sampling trains are similar.

Table 18 Comparison between the recommended and heated out-stack sampling

	Recommended system	**Heated probe, out-stack**
Isokinetic sampling	Possible, separation after the condensation	Possible, separation after the heated filter box
Filtering	Not possible due the water condensation	Possible, decomposition of some amines may occur on the filter
Sampling conditions	Temperature decrease after the nozzle. Survival of compounds unstable by heat are more probable. Condensated water in the probe liner conveys water soluble solid compounds to the drop off flask. Less contact with the sample gas.	Temperature increase after the nozzle. Heat stable compounds may decompose. Water soluble solid accumulate in the liner. Direct contact with the flue gas over the sampling period and heat may decompose compounds.
Separation of all condensate	Yes	No amount is lower due to main flow to adjustable pump. May affect on detection limits.
Maturity	Ordinary technique: All parts are used with different sampling arrangements, but not usually in this order. Not validated to CCS-plants and amines.	Ordinary technique: Standard method for example HCl sampling. Not validated to CCS-plants and amines.

7. SAMPLING PROCEDURES

7.1 Introduction

There are no standard methods available for the sampling of the amine and other related compounds from the humid flue gas. In the literature survey it was revealed that the sampling and analysis has been performed mainly from atmospheric or work place air and no studies of direct flue gas sampling were found in order to analyze the compounds of interest. Since the differences of flue gas and air, many of the presented methods are not suitable for flue gas sampling and adjustments are expected to be needed when applying the air sampling methods for flue gas.

US OSHA and NIOSH has reported and validated sampling methods for the workplace air. Methods are very similar and the absorption mediums differ depending on the compound sampled. Some problems on workplace air sampling methods compared to flue gas sampling are:

a) Sample matrix differs significantly from the flue gas, e.g. nitric oxides, CO_2 and water concentrations are much lower
b) Sampling rate may be much lower (leads to short sampling times)
c) Overall sampling capacity of the commercial industrial hygiene sampling tubes may be at low level especially at humid conditions
d) Significant head loss of some sampling tubes

However many of these problems could be avoided by proper design.

Besides the fully or partially validated standard methods by OSHA, NIOSH, EPA etc., multiple methods were found in the published articles. However, the method description in article can be rather general. In addition, since usually the article methods are not tested or evaluated by others than the authors, the method should be considered with precautions. However, some of the article methods might be very useful but are expected to need more of testing to find out the method reliability and suitability for intended purpose.

7.2 Decomposition and reactivity of studied compounds

Since some of the amine compounds related to the CCM project are susceptible for decomposition, the potential of decomposition during sampling, transporting and analysis needs to be taken account. Nitrosamines are sensitive to light, especially for UV radiation and unstable in acidic condition. Thus, the sample should be taken in neutral or alkaline matrix and stored in the dark. However, alkylamines can be sampled, for example, in acidic solvent.

Decomposition of solvent amines has been extensively studied since the wide usage of the compounds in exhaust gas treatment (Bedell 2009, Bedell et al. 2010, Supap et al. 2009, Sexton & Rochelle 2009, Lepaumier et al. 2009, Freeman et al. 2010). The main focus has been in thermal and oxidative degradation. Since the tendency for especially thermal decomposition of MEA, other solvent amines have recently been favored. During CO_2 capture, piperazine has been reported to have higher stability towards thermal degradation and oxidation when compared to MEA (Freeman et al. 2010). Since amine oxidation is understood to be catalyzed by some metals decomposition rates in presence of metals (Fe^{2+}, Cu^{2+}, Cr^{3+} and Ni^{2+}) have been studied. In presence of iron, copper or stainless steel metals the decomposition rate of MEA was considerably higher and piperazine concentration was clearly steadier during the test (Freeman et al. 2010).

Alkylamines and amides, in addition to solvent amines, have been reported to be corrosive to various metals (e.g. Al, Cu, Pb, Zn and Sn) (Bingham et al. 2001, Pohanish 2008, Pohanish 2004, Pohanish 2002). Many of the studied compounds e.g. formamide, acetaldehyde and form the group of alkylamines and solvent amines might also attack rubbers, plastics and coatings. Amides decompose in water and acetic acid has been reported to form NH_3 and acetic acid salts (Lewis 2004, Pohanish 2008).

The studied aldehydes are reactive compounds (Bingham et al. 2001, Lewis 2004, Wypych 2008, Pohanish 2008). Acetaldehyde oxidizes readily to form corrosive acetic acid. However, acetaldehyde itself is not corrosive to metals. Formaldehyde is unstable in water and air. Instability in air is caused by degradation by photochemical processes.

7.3 Sampling location and points

Sampling location and points are chosen according to EN 13284-1, refer also H&ETQPamine1, report of Sub-Task 1.

7.4 Preparation and installation of equipment

7.4.1 Advance preparations at the laboratory

All components in contact with sample gas must be cleaned prior to sampling. The cleaning will be done by thoroughly rinsing the lines and absorbers to be used with acetone, washing those with pure water at 80 °C and finally rinsing with ethanol. Drying will be done at 140°C for 2 hours.

All ends must be sealed with aluminum foil to avoid contamination.

The following measuring devices shall possess valid calibration:

- gas meters
- pitot tubes and manometers
- temperature measurement devices, both thermocouple and reader
- balances
- nozzles

Silicagel should be dry-packed and weighted at the laboratory if balance is not available at the field. The accuracy of the balance should be better than 0.5 g.

7.4.2 Preparations at the sampling site

The balance should be calibrated at the field using filed reference weight. Silicagel unit is weighted before analysis.

Leak test should be performed before sampling. Leak test shall not exceed 2 % of the expected sample gas flow rate. During the leak test it is a good practice to gently shove the sampling system to observe if there are loose connections which may open while operating the system during the actual sampling (e.g. adding ice).

NOTE: Care should be taken while ending leak test and reducing pressure from the system to avoid sudden over-flow of the liquid absorbers e.g. take off the stopper from the upstream of the sampling train prior to stop the sampling pumps.

After the leak test all transparent parts of the sampling system shall be covered by aluminum foil to avoid light to intrude into the sample.

Cooling pumps must be started before the sampling to stabilize the cooler temperature. Temperature at the cooler shall be under 20 °C; preferably under 10 °C. Direction of the cooling water flow shall run against the sample gas stream flow.

If mass spectrometry based analysis are used on analysis, accurate amount and known concentration of ^{13}C labeled nitrosamine-water solution is spiked using syringe from the tip of the sampling probe. Care should be taken to avoid outflow of spiking liquid before the sampling starts. Spiking is recommended at least in validation stage of method to estimate recovery rate and possible decomposition during sampling.

7.5 Sampling

Taking into account the expected concentration to be measured and the analytical detection limit of the available method, the required sampled volume and sampling time will be calculated.

Sampling should be taken by isokinetic method. Overall suction velocity should be measured and adjusted at any measurement point. Two sampling lines are recommended, if flow conditions are not homogeneous. Sampling line should be leak cheked when changing the sampling line.

Every observations during the sampling should be written down. Temperatures etc. shall be recoreded in, at least, every 15 minutes.

Humidity shall be calculated taking accunt overall mass increase of the sampling system (if measured) or from amount of condesate.

7.6 Sample recovery from the sample line

The samples should be stored in the dark, not higher than in room temperature (< 25 °C). Samples should be stored at glass vessels.

Inner surfaces of sampling train shall be rinsed with contaminant free water. Rinsing solution becomes part of the sample and combined with condensate. Rinsing volume is 100 ml. Last impinger shall be analysed separately to estimate break through volume.

7.7 Sample storage

The samples should be stored in the dark not higher than room temperature (< 25 °C). Samples should be stored at glass vessels.

If during the validation occurs that decomposition is major, the nitrogen bubbling though the sampling liquid could be tested to reduce oxygen content in water after the sampling. In this case samples should storage air tight containers.

Preservation chemicals, if needed, are described more detailed at the subtask 5 report.

8. SAMPLING SYSTEM FOR ALDEHYDES

Aldehydes may be possible to analyse from the sampling mediums described above. This will reveal more detailed during the subtask 5. However, alternate method is available.

Aldehyde could be sampled by US. EPA method 0011 "*Sampling from selected aldehyde and ketone emissions from stationary sources*".

Gaseous and particulate pollutants are withdrawn isokinetically from an emission source and are collected in aqueous acidic 2,4-dinitrophenylhydrazine. Formaldehyde present in the emissions reacts with the 2,4-dinitrophenylhydrazine to form the formaldehyde dinitrophenylhydrazone derivative. The dinitrophenylhydrazone derivative is extracted, solvent-exchanged, concentrated, and then analyzed by high performance liquid chromatography (HPLC) according to Method 8315 or other appropriate technique. Some other amines are possible to sample the method in question.

One challenge with post combustion flue gas is NO_2 because high levels of nitrogen dioxide can interfere by consuming all of the reagent. Normally about 90 % of NO_x are as NO and rest are N_2O and NO_2. Expected levels of NO_2 are low at amine plant because of CO_2 capture process so the method may be functional.

Sampling system is presented at the Figure 11. Sampling train for aldehydes and ketones (US EPA Method 0011)Figure 11.

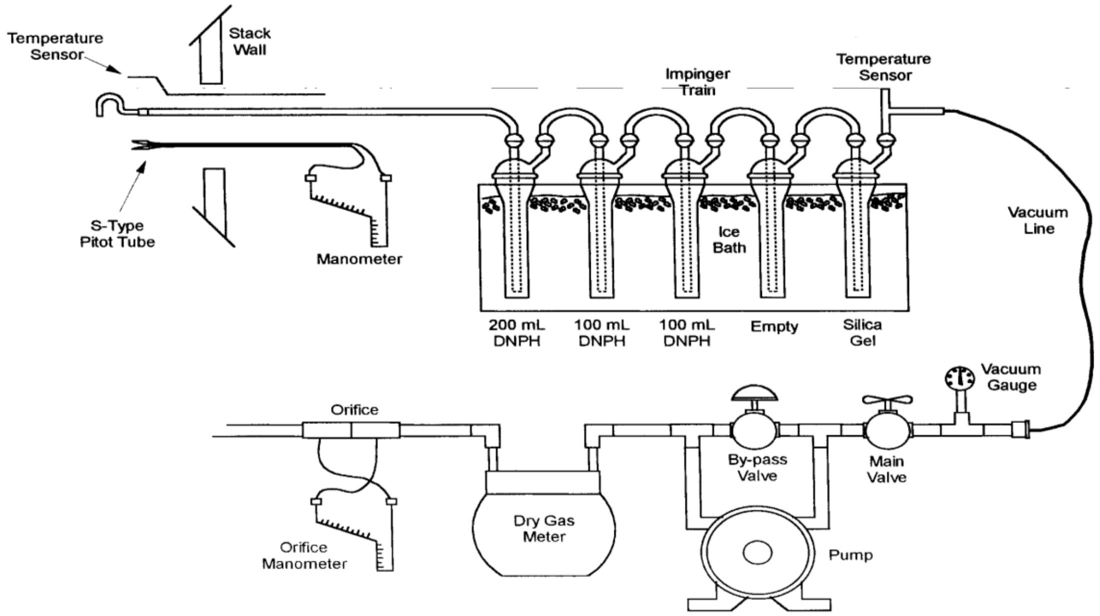

Figure 11. Sampling train for aldehydes and ketones (US EPA Method 0011)

The detailed description of the apparatus and sampling procedure is at US. EPA method 0011 chapters 4-7.

9. SAMPLING SYSTEM FOR AMMONIA

Ammonia may be possible to analyse from the sampling mediums described above. This will reveal more detailed during the subtask 5. However, alternate approach is available.

Ammonia could be sampled according to US EPA conditional test method CTM-027 "*Procedure for Collection and Analysis of Ammonia in Stationary Sources*" using sampling train described at A Method 17 sampling train is required to collect the ammonia samples. This system is described in 40 CFR Part 60, Appendix A, and in the EPA Quality Assurance Handbook for Air Pollution Measurement Systems, Volume III - Stationary Source Specific Methods, Section 3.11, January, 1982 (EPA-600/4-77-027b).

This method is validated to coal fired power plants only.

This analysis has a major disadvantage since it interferes with amines. If flue gas amine concentration is low related to ammonia, method may be used if this inconsistency is tolerated. A summary parameter of ammonia plus amine may be useful for some purposes. During the subtask 5 it may be possible to develop an analysis method based on derivatization of ammonia only. This will be described more detailed at the subtask 5 final report.

10. FURTER WORK AND RECOMMENDATIONS

- Method evaluation, i.e. is it suitable for the intended purpose. Many methods were meant for ambient and workplace air sampling, thus they might not be suitable for flue gas sampling. However, it could be possible to use the same methods with different parameters (sampling time, load of adsorbent etc.). The final stage of suitability evaluation should be done with actual testing.

- Integration with analytical method. When progressing with subtask 5 the connection between sampling and analysis becomes more evident. Since the sampling method should be integrated with analytical method, a direct recommendation of the sampling method cannot be given before the analytical methods have been completely evaluated. Thus, the suggested sampling method according to the analysis method will be reported as an amendment for subtask 5 report.
- Absorption efficiency (capacity and break through volume) and artifact formation on absorbents should be evaluated with simulated flue gas. One approach is to inject known amount of nitrosamines into sampling system followed by flush of synthetic flue gas made by bottle gases. Test gas should include NO_x, CO_2, O_2, N_2 and moisture on concentrations presented at the Table 1. Reference system is identical to the test system but flue gas is nitrogen only. Recovery of analytes should be tested by the selected methods.
- Selective ammonia and aldehyde analysis should try to extend to cover sampling arrangement presented for amines.

11. CONCLUSIONS

The aim of the sub-task 2 study was to find out the most suitable methods for CCS plant emission gas manual sampling in order to analyze amine and other related compounds. The compound groups were nitrosamines, alkyl amines, solvent amines, amides, aldehydes and ammonia. The topic was approached by means of literature survey and the suitability of the methods was evaluated. Many of the methods were standard methods i.e. by NIOSH and OSHA but also multiple article methods were found. The maturity of the methods was categorized (high, medium and low maturity) depending, if the method was for example fully validated standard, partially validated standard or article method. Also some evaluations of the method suitability and pros/cons were made.

Even though multiple sampling methods (standards and articles) for different compound groups are presented, only some of them were directly suitable for flue gas sampling. Thus these methods, mainly for ambient air, need to be modified to fit them for flue gas sampling. The methods consisted of different sampling systems, mainly impingers and other liquid phase sampling systems and variety of solid sorbent materials. The method testing is also expected to be required prior to final selection of the method, especially since the flue gas is remarkably different from the air matrices presented in the literature.

Even though it would be convenient to sample all different compounds at once, it may reveal to be impossible. Different materials have been used for almost all compound groups. One reason is the susceptibility for decomposition. For example, the nitrosamines including many so called priority compounds (in the context of the CCM project) are unstable in acidic environment but the alkylamines (also important group) are not considered to be prone to such degradation and for example acidic solvents can be used in sampling. Some congruent sampling materials were also found, i.e. XAD-2 resin seems to be suitable at least for amine and aldehyde sampling.

The mostly used sampling methods for different compound groups are presented below. The fully validated standard methods should be favored since the higher maturity, i.e. the method is expected to be more readily usable since the complex validation procedure. However, it should be noted that the methods are not directly for CCS-plant flue gas sampling.

- **Nitrosamines:** According to the literature survey the most used method employs Thermosorb/N cartridges. Also vitamin E and C treated Florisil adsorbent and Gelman Type A glass fiber filters are suitable for nitrosamine sampling

- **Alkylamines:** HCl absorption has been a usable method for sampling. Also XAD-7 resins might be applicable

- **Solvent amines:** XAD-2 resins have been extensively used in solvent amine sampling. Also an impinger with hexasulfonic acid has been presented for a sampling method

- **Amides:** Silica gel might be a proper sampling material for amides. Also other solid sorbents, such as Tenax, might be suitable
- **Aldehydes:** According to literature survey, DNPH coated silica and XAD-2 resin are the most used sampling materials
- **Ammonia:** For ammonia sampling sulphuric acid (liquid or treated carbon/silica gel) might be the method of choice

The sampling method should be integrated with the analytical method since both of them are more or less dependent of each other. The method suitability cannot be evaluated by paper only and some testing is expected to be required (especially in case of article methods). Since the analysis method development is currently in the early phase and the most suitable method is not known yet, the sampling method cannot be selected. However, recommended sampling method at the chapter 6 is a good starting point for the method development, since it will not disturb sample.

Besides the sampling materials, other factors related to reliable sampling that should be taken account are:

- If the sampled gas is expected to contain water drops or droplets, isokinetic sampling method is recommended. If droplets are not presented, sampling and equipments in practice are much easier.
- Because some of the amines may decompose by heat, water or oxidation, heated parts on sampling system are not recommended with exception of very cold weather conditions to avoid freezing. Heating at moderate temperatures (< 120 °C) may be possible
- All the materials in sampling system (and possible sorbents) in contact with the sample have to be inert, i.e. not to react with the sampled compounds

12. REFERENCES

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OSHA, d. *OSHA- Method no. 164. Ammonia in Workplace Atmosphere.*

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OSHA, g. *OSHA- Method no. 2084. Acetamide.*

OSHA, h. *OSHA- Method no. 27. Volatile Nitrosamine Mixture I.*

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OSHA, j. *OSHA- Method no. 34. Dimethylamine.*

OSHA, k. *OSHA- Method no. 36. Ethylamine.*

OSHA, l. *OSHA- Method no. 40. Methylamine.*

OSHA, m. *OSHA- Method no. 41. Diethylamine.*

OSHA, n. *OSHA- Method no. 52. Acrolein and/or Formaldehyde.*

OSHA, o. *OSHA- Method no. 60. Ethylenediamine (EDA), Diethylenetriamine (DETA), Triethylenetetraamine (TETA).*

OSHA, p. *OSHA- Method no. 68. Acetaldehyde.*

OSHA, q. *OSHA- Method no. PV2018. Diethanolamine.*

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