Document Front-page

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SUMMARY

The scope of this literature research was to present analytical methods for solvent amines and their degradation products in CO_2-capture units. Several components with possible environmental impact have been identified among the products of degradation of solvent amines. N-nitrosamines and low molecular weight (LMW) alkylamines were the main focus of this literature research. Analytical methods for solvent amines, LMW amides, aldehydes and ammonia were also studied. The matrices of interest were the treated flue gas from the absorber column (flue gas), the wash water from the absorber top (wash water) and the rich and lean aqueous amine solution circulating in the absorber (rich/lean amine solvent).

Analytical methods were searched for air/gas samples, water matrices and amine solvents. However, the flue gas is expected to be very different from for example working air but the applicability concerns mainly sampling methods (sub-task 2) and the possible complications are expected to be solved. The analysis methods for water were assumed to suit for wash water. Rich/lean amine solvent was more complex and only very little material was found in the literature that was directly related to it. Information is available on the analysis of the solvent amines, which are present in considerable amounts, in rich/lean amine solvent. The real problem of rich/lean amine solvent is the simultaneous determination of the solvent amines and their degradation products that are present as trace compounds. However, it might be possible to use water methods for rich/lean amine solvent analysis if proper pretreatment method can be defined.

Chromatographic methods, in particular gas chromatographic (GC) and liquid chromatographic (LC) methods equipped or coupled with suitable detectors i.e. mass spectrometer (MS), tandem MS (MS/MS) or high resolution MS (HRMS), were found to be the most suitable methods for the quantitative and screening analysis of the compound of interest at trace levels in both air and aqueous matrices. The methods are expected to be applied also for rich/lean amine solvent samples. For group method, less specific metods/detectors can be applied.

List of symbols and abbreviations

2-HMP	2-(hydroxymethyl) piperidine
AC	Activated Carbon
ACN	Acetonitrile
AMP	2-Amino-2-methyl-1-propanol
ASTM	American Society for Testing and Materials
BEHPA	Bis-2-ethylhexylphosphate
BGE	Background electrolyte
CAR/PDMS	Carboxen / polydimethylsiloxane
CE	Capillary Electrophoresis
CF	Concentration Factor
CI	Chemical Ionization
CIE	Capillary Ion Electrophoresis
CL	Chemiluminescence
CLD	Chemiluminescence detector
CSPE	Cartridge Solid-Phase Extraction
DAD	Photodiode Array Detector
DCM	Dichlorometane
DEA	Diethanolamine
DEN	Diethylamine
DETA	Diethylenetriamine
DIPA	Diisopropanolamine
DMA	Dimethylamine
DMNTH	4-N,N-dimethylamino-6-(4´-methoxy-1´-naphtyl)-1,3,5-triazine-2-hydrazine
DMQC-OSu	2, 6-dimethyl-4-quinolinecarboxylic acid N-hydroxysuccimide ester
DNB	Dinitrobenzoyl chloride
DNPH	2,4-dinitrophenylhydrazine
Dnpz	1,4-Dinitrosopiperazine
Dns-Cl	Dansyl chloride
DNSH	Dansylhydrazine
DSD	Diffusing Sampling Device
DVB-PDMS	Divinylbenzene-polydimethylsiloxane
EA	Ethylamine
ECD	Electron Capture Detector
EDA	1,2-Diaminoethane
EI	Electron Impact
EPA	US Environmental Protection Agency
ESI	Electrospray Ionization
FAIMS	High-Field Asymmetric Waveform Ion Mobility Spectrometry
FID	Flame Ionization Detector
FL	Fluorescence Detector
FMOC	9-fluorenylmethyl chloroformate
FPD	Flame Photometric Detector
GC	Gas Chromatography
HBA	4-hydrazinobenzoic acid
HPLC	High Performance Liquid Chromatography
HRMID	High Resolution Multiple-Ion Detection
HRMS	High Resolution Mass Spectrometer
HS	Head Space
IBCF	Isobutyl chloroformate
IC	Ion Chromatography
I.D or i.d. or id	Internal diameter
ISO	International Organization for Standardization
LC	Liquid Chromatography
LIF	Laser Induced Fluorescence detector
LLE	Liquid-Liquid Extraction

LMW	Low Molecular Weight
LOD	Limit of Detection
LOQ	Limit of Quantification or Quantitation
LRQ	Reliable Quantitation Limit
MCPBA	5-isothiocyanato-1,3-dioxo-2-p-tolyl-2,3-dihydro-1H-benz[de]isoquinoline
MDEA	N-Methyldiethanolamine
MDL	Method Detection Limit
MDMNTH	N-Methyl-4-N´,N´-dimethylamino-6-(4´-methoxy-1´-naphthyl)-1,3,5-triazine-2-hydrazine
MEA	Monoethanolamine
MEKC	Micellar Electrokinetic Capillary Chromatography
MLLE	Micro Liquid-Liquid Extraction
MMA	Methylamine
MRM	Multiple Reaction Monitoring
MS	Mass Spectrometer
MW	Molecular Weight
NBD-Cl	4-chloro-7-nitro-2,1,3-benzoxadiazole (NBD Chloride)
NBD-F	4-fluoro-7-nitrobeno-2-oxa-1,3-diazole
NCD	Nitrogen Chemiluminescence Detector
NDA	Naphthalene-2,3-dicarboxaldehyde
NDBA	N-Nitrosodi-n-butylamine
NDEA	N-Nitrosodiethylamine
NDELA	N-Nitrosodiethanolamine
NDMA	N-Nitrosodimethylamine
NDPA	N-Nitrosodi-n-propylamine
NIOSH	US National Institute for Occupational Safety and Health
NIT or NITC	1-naphtylisothiocyanate
NMOR	N-Nitrosomorpholine
NOC	Nitroso Organic Compounds
NPD	Nitrogen-Phosphorous Detector
NPIP	N-Nitrosopiperidine
NPYR	N-Nitrosopyridine
NPRO	N-Nitrosoproline
o.d.	Outer Diameter
OPA	Phthalaldehyde
OSHA	US Occupational Safety and Health Administration
PAD	Pulsed Amperometric Detector
pCEC	Pressure Assisted Capillary Chromatography
PCI	Positive Chemical Ionization
PDMS	Polydimethylsiloxane
PED	Pulsed Electrochemical Detector
PFB	Pentafluorobenzoyl
PFBHA	*o*-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine hydrochloride
PFBOA	*o*-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine
PFPH	2,3,4,5,6-pentafluorophenyl hydrazine
pK_a	Acid dissociation constant
pK_b	Basic dissociation constant
PNICI	Positive and Negative Ion Chemical Ionization
PTFE	Polytetrafluoroethylene
RCC	Reactive Carbonyl Compound
Ref.	Reference
RI	Refractive Index
RID	Refractive Index Detector
RP	Reverse Phase
RQL	Reliable Quantitation Limit
RRF	Relative Response Factors
RSD	Relative Standard Deviation
SCOT	Support-coated open-tubular

SIFA	N-hydroxysuccinimidyl fluorescein-O-acetate
SIPA	N-hydroxysuccinimidyl phenylacetate
SIM	Single Ion Monitoring
SPE	Solid-Phase Extraction
SPME	Solid-Phase Micro Extraction
TANC	Total Apparent N-nitroso Compounds
T_b	Boiling point
TCECF	Tricloroethyl chloroformate
TD	Thermal Desorption
TEA	Thermal Energy Analyser
TEA	Triethylamine
TETA	Triethylenetetramine
TLC	Thin Layer Chromatography
TMA	Trimethylamine
TNC	Total N-nitroso Compounds
TRIS	Tris(hydroxylmethyl)aminomethane
TSD	Thermionic Specific Detector
UPLC	Ultra Performance Liquid Chromatography
UV	Ultraviolet
VIS	Visible Detector
VOC	Volatile Organic Compounds
Wt%	Weight %

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1. INTRODUCTION

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

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

The purpose of this literature research is to present methods of analysis for solvent amines and their degradation products formed in amine-based CO_2-capture processes. The components of special interest are N-nitrosamines and low molecular weight alkylamines. Analytical methods are also presented for solvent amines, low molecular weight amides and aldehydes. The sample matrices are the treated flue gas from the absorber column, the wash water from the absorber top and the rich and lean aqueous amine solution circulating in the absorber.

All the compounds are treated as trace compounds, with the exception of the solvent amines in rich/lean amine solvent. For N-nitrosamines, not only quantitative but also screening and group methods are included in this work. The main characteristics and the applicability of each analytical method are presented in table form. Most of the analytical methods included in this work are from literature publications, especially in the case of N-nitrosamines, that due to their carcinogenicity are wildly researched. US OSHA (Occupational Safety and Health Administration), NIOSH (National Institute for Occupational Safety and Health) and EPA (Environmental Protection agency) methods are included. The existence of ISO (International Organization for Standardization) and ASTM (American Society for Testing and Materials) suitable standard methods is also investigated.

2. COMPOUNDS OF INTEREST AND THEIR PROPERTIES

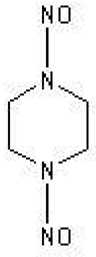
The compounds of interest in this study are the amines present in the unit as solvent and their degradation products. The compounds are divided according to the chemical group to which they belong. They are listed in alphabetical order within each group.

2.1 Nitrosamines

Nitroso compounds are formed by the action of a nitrous group on a nitrogen group. Some nitrosamines have been used in the rubber industry, where toxicity effects on workers' livers were observed. For this reason studies were conducted on the relationship between n-nitrosamines and human carcinogenesis. It was found that a large amount of nitrosamines are carcinogenic. Nitrosamines can be volatile or non-volatile. Volatile nitrosamines are those in which the alkyl side chains are simple unsubstituted hydrocarbon chains or simple aromatic substituents.

Nitroso compounds can be analyzed as a group and described as TNC (Total N-nitroso Compounds) or as TANC (Total Apparent N-nitroso Compounds), in which case they have been analyzed by a group reaction which assays the number of N-nitroso bonds without giving information on the type of N-nitroso compounds. Total volatile N-nitroso compounds include the compounds that can be detected by gas chromatography. In some studies, only the N-nitroso amino acids found in normal human urine are referred to as non-volatile N-nitroso compounds (Hill 1996).

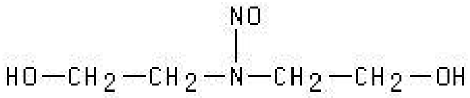
2.1.1 1,4-Dinitrosopiperazine (Dnpz)



Other names: N,N'-dinitrosopiperazine, dinitrosopiperazine, NSC 339, USAF do-36, Dnpz.

Dinitrosopiperazine is a solid shaped as white/cream colored crystals. It is miscible in water, acetone and hot ethanol. The melting point is 158 °C. It is considered to be non-volatile since it has low vapor pressure (Calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (1994-2010 ACD/Labs) (Lewis 2004, Gangolli 2005)).

2.1.2 N-Nitrosodiethanolamine (NDELA)

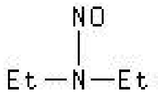


$$HO-CH_2-CH_2-\overset{\overset{NO}{|}}{N}-CH_2-CH_2-OH$$

Other names: nitrosobis-(2-hydroxyethyl)-amine, bis(b-hydroxyethyl)nitrosamine, diethanolnitrosoamine, 2,2'-dihydroxy-N-nitrosodiethylamine, 2,2'-iminodi-N-nitrosoethanol, N-nitrosoaminodiethanol, N-nitrosodiethanolamine, 2,2'-(Nitrosoimino)bisethanol.

NDELA is a pale yellow viscous liquid. It is miscible with water in all proportions (solubility 1 g/l). NDELA is soluble in polar organic solvents and insoluble in non polar organic solvents. It is odorless and almost non volatile (vapor pressure 7×10^{-5} kPa at 20°C). NDELA is sensitive to light, especially UV light. It is stable at room temperature in neutral or alkaline solutions in the dark, but less stable in acidic solutions. NDELA decomposes at 200°C (Bingham et al. 2001, Gangolli 2005, Prager 1998).

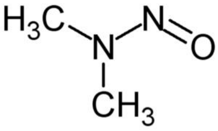
2.1.3 N-Nitrosodiethylamine (NDEA)



Other names: diethylnitrosamine, DANA, DEN, DENA, N,N-diethylnitrosamine, N,N-diethylnitrosoamine, N-ethyl-N-nitrosoethanamine, N-nitroso-N,N-diethylamine, nitrosodiethylamine.

NDEA is pale yellow liquid. It is soluble in water but not completely miscible. Its water solubility is about 10%. The chemical in excess will form a layer on top of the water (density 0.942 g/l at 20°C). NDEA is soluble in alcohols and ethers. Like NDMA and NDELA, it is stable in neutral and alkaline solution but unstable in acid solution and in light, which slowly decomposes it. A vapor pressure of 0.1 kPa at 20°C was reported (Lewis 2004, Bingham et al. 2001, Pohanish 2008, Prager 1998).

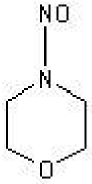
2.1.4 N-Nitrosodimethylamine (NDMA)



Other names: N-methyl-N-nitrosomethanamine, dimethylnitrosamine, N,N-dimethylnitrosamine, dimethylnitrosoamine, DMN, DMNA.

NDMA is a very pale yellow liquid. It is miscible with water and most organic solvents, like alcohols and ethers. Similarly to NDELA and NDEA, NDMA hydrolyses slowly in acid solutions but it is stable in neutral and alkaline solutions. Also NDMA slowly decomposes when exposed to light, especially in aqueous solutions. The flash point is 61 °C and the vapor pressure at 20 °C is 0.36 kPa (Lewis 2004, Wypych 2008, Bingham et al. 2001, Pohanish 2008, Gangolli 2005).

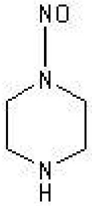
2.1.5 N-Nitrosomorpholine (NMOR)



Other names: 4-nitrosomorpholine, nitrosomorpholine.

Nitrosomorpholine is a low melting yellow solid. The melting point is 29°C. The boiling point of NMOR is reported as 96°C (6mm) in (Bingham et al. 2001), while other sources (Gangolli 2005, Verschueren 2001) report a boiling point of 224-224.5°C. NMOR is miscible with water and soluble in organic solvents such as diethyl ether and ethanol. Nitrosomorpholine is a little unstable in the light and in acidic solutions, while it is stable in neutral and alkaline solutions (Lewis 2004, Bingham et al. 2001, Gangolli 2005, Verschueren 2001).

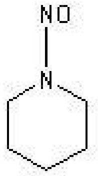
2.1.6 N-Nitrosopiperazine



Other names: Mononitrosopiperazine, 1-nitrosopiperazine

There are no other physical and chemical data available on this compound than those reported in Table 1. It is suspected to be carcinogen and when heated to decomposition it emits toxic fumes such as NO_x (Lewis 2004).

2.1.7 N-Nitrosopiperidine (NPIP)



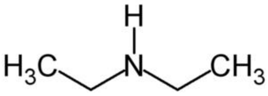
Other names: hexahydro-N-nitrosopyridine, 1-nitrosopiperidine, N-N-PIP, NO-PIP, N-nitroso-piperidin, nitrosopiperidine, hexahydro-N-nitrosopyridine.

NPIP is light yellow oil. It is soluble in water (77 g/l), in organic solvents such as acetone, diethyl ether and ethanol and very soluble in acid solutions. The flash temperature is 93°C. Like many other nitrosamines, NPIP is stable in neutral and alkaline solution, but somewhat unstable in acid solution and in light. NPIP is a volatile nitrosamine (Lewis 2004, Bingham et al. 2001, Pohanish 2008, Gangolli 2005, Pohanish 2002).

2.2 Alkylamines

Alkylamines are amines with substituted alkenes. The lower alkylamines are monomethylamine, dimethylamine and trimethylamine. Higher alkylamines correspond e.g. to the $R–CH_2–NH_2$ type (Rouette 2001).

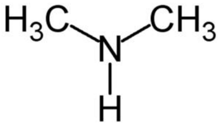
2.2.1 Diethylamine (DEN)



Other names: N-ethylethanamine, N-ethyl ethanamine, N,N-diethylamine, 2-aminopentane, diethamine.

Diethylamine is a colorless flammable liquid classifiable as carcinogen. It is soluble in water and alcohol. Diethylamine is strongly alkaline (pH 13) and corrosive, it attacks aluminum, copper, lead, tin, zinc and alloys. The melting point is -50°C and the flash point is -23°C. The autoignition temperature is 312°C. The vapor pressure of diethylamine at 20°C is 25.6 kPa (Lewis 2004, Wypych 2008, Pohanish 2004, Bingham et al. 2001, Pohanish 2008, Verschueren 2001, Pohanish 2002).

2.2.2 Dimethylamine (DMA)



Other names: N,N-dimethylamine, dimethylamine anhydrous, N-methylmethanamine

DMA is a colorless flammable gas at room temperature and atmospheric pressure. It is liquid below 6.9°C (a boiling point of 7.4°C is reported (Verschueren 2001)). DMA is a medium-strong base and it is corrosive. It attacks aluminum, copper, lead, tin, zinc and alloys, some plastics, rubbers and coatings. It is soluble in water (solubility in water of about 24 % at 60°C). A saturated water solution has a pH of 14. It is soluble also in alcohol and ether. The freezing point is -92.2°C and the flash point is -17.7°C. The autoignition temperature is 430°C (anhydrous) according to (Lewis 2007) and 401°C according to (Pohanish 2008). The vapor pressure is 172 kPa at 20°C (Lewis 2004, Wypych 2008, Pohanish 2004, Bingham et al. 2001, Pohanish 2008, Lewis 2007, Prager 1998, Verschueren 2001).

2.2.3 Ethylamine (EA)

Other names: ethanamine, aminoethane, MEA, monoethylamine, 1-aminoethane.

Ethylamine is a colorless flammable gas or water-white liquid (below 17°C). EA is miscible in water, alcohol and ether and it is salted out by NaOH. The aqueous solution is a strong base. EA is corrosive. It attacks nonferrous metals like aluminum, copper, lead, tin, zinc and alloys, some plastics, rubber and coatings. The freezing point is -81°C, the flash point is -18°C and the autoinition temperature is 385°C. The vapor pressure is 113-122 kPa at 20°C (Lewis 2004, Wypych 2008, Pohanish 2004, Bingham et al. 2001, Pohanish 2008, Verschueren 2001, Pohanish 2002).

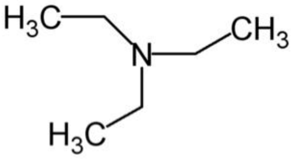
2.2.4 Methylamine (MMA)

$H_2N—CH_3$

Other names: methanamine, aminomethane, monomethylamine anhydrous, monomethylamine.

Methylamine is a colorless flammable poisonous gas (liquid below 6°C). It is very soluble in water (1 080 g/kg) and is therefore often encountered as a 25-48% aqueous solution. It is soluble in alcohol and miscible with ether. The flash point is -10°C, the freezing point is -93°C and the autoignition temperature is 430°C. It is a medium-strong base corrosive to copper, zinc alloys, aluminum, and galvanized surfaces. The vapor pressure is 314 kPa at 20°C (Lewis 2004, Wypych 2008, Pohanish 2004, Bingham et al. 2001, Verschueren 2001, Pohanish 2002, Pohanish 2002).

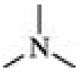
2.2.5 Triethylamine (TEA)



Other names: N,N-diethylethanamine, diethylaminoethane, TEN.

TEA is a colorless, flammable, volatile liquid that produces a large amount of vapor. It is slightly soluble in water (170 g/kg) above 18.7°C and miscible below this temperature. It floats on water surface. TEA is miscible with alcohol and ether, e.g. diethyl ether and ethanol. The freezing point is -114.7°C, the flash point is between -7°C and -9°C and the autoignition temperature is 250°C. The vapor pressure is 6.6 kPa at 20°C. It is a strong base corrosive to aluminum, zinc, copper, and their alloys in the presence of moisture (Wypych 2008, Pohanish 2004, Bingham et al. 2001, Lewis 2007, Gangolli 2005, Verschueren 2001, Pohanish 2002).

2.2.6 Trimethylamine (TMA)



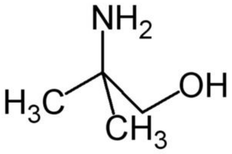
Other names: N,N-dimethylmethanamine.

TMA is a flammable, alkaline, colorless gas at ambient temperature and atmospheric pressure. It is shipped as compressed gas or an aqueous solution. It is soluble in water (48 % at 30°C), ether, benzene, toluene, xylene, ethylbenzene, and chloroform. TMA is a medium-strong base corrosive to many metals such as zinc, brass, aluminium, copper, tin and their alloys. The melting point is 117°C and the autoignition temperature is 190°C. The vapor pressure at 21°C is 194 kPa (Pohanish 2004, Bingham et al. 2001, Pohanish 2008, Pohanish 2002).

2.3 Solvent amines

Amines, mostly alkanolamines (compounds with amino and hydroxyl groups on alkane backbone), are traditionally used in aqueous solutions as solvents in gas sweetening units, where carbon dioxide and hydrogen sulfide are stripped from natural gas. Amines show variable toxicity, many are skin irritants and some are sensitizers (Lewis 2004).

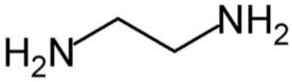
2.3.1 2-Amino-2-methyl-1-propanol (AMP)



Other names: isobutanolamine, 2-aminodimethylethanol, β-aminoisobutanol, AMP-95, isobutanol-2-amine.

AMP is a thick colorless liquid or crystalline solid. It is miscible in water and it is corrosive. The pH is 11.3. The freezing point is 31°C and the flash point is 67°C. AMP shows low volatility (vapor pressure 0.133 kPa at 20°C) (Wypych 2008, Pohanish 2004, Knovel 2003).

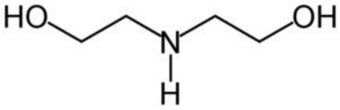
2.3.2 1,2-Diaminoethane (EDA)



Other names: ethylenediamine, dimethylenediamine, aminoethylamine, 1,2-ethanediamine, 1,2-ethylenediamine.

EDA is a poly amine. It is a highly flammable, clear colored, hygroscopic, fuming thick liquid. EDA is miscible in water (initially floats on the surface of water) and alcohol. It is corrosive and a medium strong base. EDA attacks aluminum, copper, lead, tin, zinc and alloys, some plastics, rubber and coatings. The freezing point is 8.5°C and the flash point is 33.9°C. The vapor pressure is 1.5 kPa at 20°C. EDA forms explosive mixture with air (Wypych 2008, Pohanish 2004, Bingham et al. 2001, Pohanish 2008).

2.3.3 Diethanolamine (DEA)

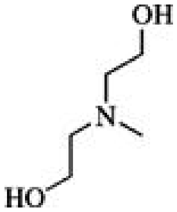


Other names: 2-(2-hydroxyethylamino) ethanol sulfate, bis-(beta-hydroxyethyl)-amine, 2,2′-iminodiethanol, 2,2′-dihydroxydiethylamine, bis(2-hydroxyethyl)amine, diethylolamine, di(2-hydroxyethyl)amine, diolamine, 2,2- iminobisethanol.

Diethanolamine is a hygroscopic colorless crystalline solid or a syrupy, white liquid above 28 °C. DEA is highly soluble in water (95 %). It is corrosive to copper, zinc, aluminum and their alloys, and galvanized iron. The aqueous solution is a medium strong base. The flashing point is 137.4°C and DEA is reported to decompose at boiling point. It is almost non volatile, having a vapor pressure lower than 0.001 kPa at 20°C. DEA reacts with CO_2 in the air.

Aqueous solutions of diethanolamine (DEA) have been used for many years for stripping CO_2 and H_2S from refinery gases also containing COS and CS_2 in great amounts. DEA, being a secondary amine, is less reactive with COS and CS_2 than primary amines and the products of their reactions are not particularly corrosive. DEA undergoes numerous irreversible reactions with COP that form corrosive degradation products. Therefore, DEA may not be the best choice for treating gases with a high CO_2 content (Lewis 2004, Wypych 2008, Bingham et al. 2001, Pohanish 2008, Kohl & Nielsen 1997).

2.3.4 N-Methyldiethanolamine (MDEA)

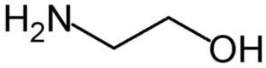


Other names: monoethyldiethanolamine, 2,2'-methyliminodiethanol, methyldiethanolamine, N-methyliminodiethanol, N-methyl-2,2'-iminodiethanol.

MDEA is a colorless combustible liquid. It is miscible with water and benzene. The melting point is -23°C and the flash point is 126°C. It is almost non volatile, having a vapor pressure lower than 0.001 kPa at 20°C.

MDEA is mostly used in the selective absorption of hydrogen sulfide in presence of carbon dioxide where the ratio of carbon dioxide to hydrogen sulfide is very high. MDEA can be used in concentrations up to 60 wt% in aqueous solutions without appreciable evaporation losses. In addition, MDEA is highly resistant to thermal and chemical degradation, and it is essentially noncorrosive. MDEA has low specific heat and heats of reaction with H_2S and CO_2 and it is only sparingly miscible with hydrocarbons (Pohanish 2004, Bingham et al. 2001, Kohl & Nielsen 1997, Lewis 2007).

2.3.5 Monoethanolamine (MEA)

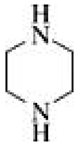


Other names: 2-aminoethanol, beta-aminoethyl alcohol, aminoethanol, ethanolamine, 2-N-ethyaminoethanol, 2-hydroxyethylamine, EA, beta-aminoethanol, colamine, beta-ethanolamine, glycinol, beta-hydroxyethylamine, olamine, thiofaco m-50, 2-ethanolamine, 2-hydroxyethanamine, 2-amino-1-ethanol, 1-amino-2-hydroxyethane, hydroxyethylamine.

MEA is a colorless thick, oily, viscous liquid. MEA initially sinks in water but it is completely soluble. The melting point is 10.6°C and the flash point is 85°C. MEA is a medium-strong base and it may attack copper, aluminum and their alloys and rubber. It also reacts with iron. MEA volatility is low (vapor pressure about 0.07 kPa at 20°C).

Aqueous solutions of MEA were almost exclusively used for many years for the removal of H_2S and CO_2 from natural and certain synthesis gases. MEA has now been mostly replaced by other alkanolamines. MEA has a low molecular weight; therefore high solution capacity at moderate weight concentrations is achievable. Aqueous solutions of MEA are highly alkaline and can easily be purified from contaminants. MEA undergoes irreversible reactions with COS and CS_2 resulting in high chemical losses. MEA solutions are more corrosive than solutions of the most other amines, particularly if the amine concentrations exceed 20% and the solutions are highly loaded with acid gas. MEA has a high heat of reaction with CO_2 and H_2S. Its vapor pressure is higher with respect to other amines, causing significant vaporization losses especially at low pressures. This difficulty can be overcome by a water wash treatment of the purified gas (Wypych 2008, Pohanish 2004, Pohanish 2008, Kohl & Nielsen 1997).

2.3.6 Piperazine



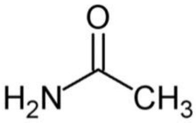
Other names: hexahydropyrazine, diethylenediamine, piperazidine, antiren, 1,4-diethylenediamine, N,N-diethylene diamine (Dot), dispermine, hexahydro-1,4-diazine, lumbrical, piperazine anhydrous, pyrazine hexahydride.

Piperazine is a transparent, deliquescent solid. The solid is combustible but does not ignite easily. The melting point is 106°C and the flash point is 82°C (anhydrous) and 87°C (hexahydrate). Piperazine is very soluble in water, glycerine and glycols but insoluble in ethers. Aqueous solutions of piperazine are strongly alkaline ($pK_b = 4.19$); the pH of a 10% aqueous solution is 11. Piperazine attacks aluminum, copper, nickel, magnesium and zinc. The vapor pressure of piperazine is less than 0.13 kPa at 20°C (Pohanish 2004, Bingham et al. 2001, Pohanish 2008, Lewis 2007).

2.4 Amides

Amides are organic compounds that contain the structural group $-CONH_2$. Common examples are acetamide, formamide and urea. Most of the saturated amides have low toxicity. The unsaturated and N- substituted amides are irritant and can be absorbed via skin contact causing injury to liver, kidney, and brain (Lewis 2004).

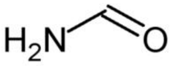
2.4.1 Acetamide



Other names: ethanamide, acetic acid amide, methanecarboxamide, acetimidic acid.

Acetamide is colorless to yellow deliquescent, crystalline solid. The melting point is 81°C. It is soluble in water (2 000 g/kg). It is reported to be corrosive (Wypych 2008). It has beens stated that acetamide decomposes in hot water (Lewis 2004) and that it decomposes slowly in cold water (Pohanish 2008). In contact with water it hydrolyses to ammonia and acetate salts. The vapor pressure at 65°C is 0.133kPa. Acetamide is a suspected carcinogen (Lewis 2004, Wypych 2008, Pohanish 2008, Verschueren 2001, Pohanish 2002).

2.4.2 Formamide



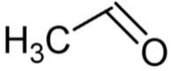
Other names: carbamaldehyde, formic acid amide, methanamide

Formamide is a colorless, viscous liquid. It is soluble in water (pH: 7.3), where it reacts slowly forming ammonium formate. It is miscible in methanol and very slightly soluble in ethanol. Formamide is hygroscopic, i.e. it absorbs moisture from the air. The melting point is 2.5°C, the flash point is 154°C and the autoignition temperature is 150°C. Formamide decomposes when heated at 180°C forming ammonia, water, carbon monoxide and hydrogen cyanide. Toxic products of combustion may include anhydrous ammonia, CO_2, prussic acid, and nitrogen oxides. Formamide attacks metals, such as aluminum, iron, copper, brass, lead, and natural rubber. The vapor pressure at 30°C is 0.01 kPa (Lewis 2004, Wypych 2008, Pohanish 2004, Pohanish 2008, Verschueren 2001, Pohanish 2002).

2.5 Aldehydes

Aldehydes are a class of chemicals characterized by the unsaturated carbonyl group. Aldehydes are used in many industrial processes. Formaldehyde and acetaldehyde are carcinogens and many other aldehydes are mutagens. The lower aldehydes are very soluble in water while the higher aldehydes are much less soluble (Lewis 2004).

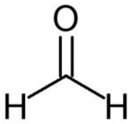
2.5.1 Acetaldehyde



Other names: ethanal, ethyl aldehyde, acetic aldehyde, acetylaldehyde, aldehyde C(2).

Acetaldehyde is a colorless flammable liquid and very soluble in water and in most common organic solvents such as alcohol, ether, benzene, gasoline, solvent naphtha, toluene, xylenes, turpentine and acetone. Mixtures of 30-60% acetaldehyde vapor in the air ignite at temperatures lower than 100°C. Acetaldehyde is a highly reactive compound. It oxidizes readily to form corrosive acetic acid. Rubber products decompose on contact with acetaldehyde, but it is not corrosive to most metals. The melting point of acetaldehyde is 123.5°C, the flash point is –38°C and it decomposes above 400°C to form principally methane and carbon monoxide. The vapor pressure of acetaldehyde is 101 kPa at 20°C (Wypych 2008, Bingham et al. 2001).

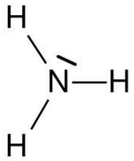
2.5.2 Formaldehyde



Other names: formalin, methylene oxide, methyl aldehyde, methanal, formic aldehyde, oxomethane, formol, oxymethylene, morbicid, veracur, methylene glycol, formalin 40, BFV, fannoform, formalith, FYDE, HOCH, karsan, lysoform, superlysoform, oxomethylene, methan 21, melamine-formaldehyde resin.

Formaldehyde is a flammable colorless gas at room temperature and pressure. Pure formaldehyde is not available due to its tendency to polymerize. It is usually sold either as a solid polymer (paraformaldehyde) or in aqueous solutions stabilized by small amounts of methanol (formalin, 37% formaldehyde). It is readily soluble in water (solubility 400 g/kg), alcohols, ketones, ether, acetone, chlorinated and aromatic hydrocarbons, and other organic solvents and it is slightly soluble in pentane, petroleum ether, and lower paraffins. Formaldehyde has a short half-life in air because it is degraded by photochemical processes and it is unstable in water. The boiling point of the 37% commercial solution, formalin, is 101°C. The melting point is -92.2°C and the autoignition temperature is 430°C (Lewis 2004, Wypych 2008, Bingham et al. 2001, Pohanish 2008).

2.5.3 Ammonia



Ammonia is a colourless gas (at room temperature and pressure) with a characteristic pungent odour. Ammonia is stable at room temperature. Anhydrous ammonia will react exothermically with acids and water and it has potentially explosive reactions with strong oxidizers. Anhydrous ammonia decomposes to hydrogen and nitrogen gases above 450°C. The vapour pressure at 21°C is 786 kPa (MSDS anhydrous ammonia, 2005).

Table 1 Compounds and their properties.

Compound	CAS-number	Formula	MW (g/mol)	T_b (°C)	pK_a	Reference
Nitrosamines						
Dnpz	140-79-4	$C_4H_8N_4O_2$	144.13	158		(Gangolli 2005)
NDELA	1116-54-7	$C_4H_{10}N_2O_3$	134.1	114		(Bingham et al. 2001)
NDEA	55-18-5	$C_4H_{10}N_2O$	102.1	177		(Bingham et al.2001)
NDMA	62-75-9	$C_2H_6N_2O$	74.08	154		(Wypych 2008)
NMOR	59-89-2	$C_4H_8N_2O_2$	116.1	224		(Gangolli 2005, Verschueren 2001)
N-Nitrosopiperazine	5632-47-3	$C_4H_9N_3O$	115.16	85-95		(Lewis 2004, Berg 1959)
NPIP	100-75-4	$C_5H_{10}N_2O$	114.15	100		(Bingham et al. 2001)
Alkylamines						
DEN	109-89-7	$C_4H_{11}N$	73.14	55	10.5	(Wypych 2008)
DMA	124-40-3	C_2H_7N	45.08	7		(Lewis 2007)
EA	75-04-7	C_2H_7N	45.1	16	10.81	(Wypych 2008)
MMA	74-89-5	CH_5N	31.07	-6	10.66	(Wypych 2008)
TEA	121-44-8	$C_6H_{15}N$	101.22	89	10.78	(Wypych 2008)
TMA	75-50-3	C_3H_9N	59.11			(Bingham et al. 2001)
Solvent amines						
AMP	124-68-5	$C_4H_{11}NO$	89.14	165	9.72	(Wypych 2008)
DEA	111-42-2	$C_4H_{11}NO_2$	105.14	269	8.96	(Wypych 2008)
EDA	107-15-3	$C_2H_8N_2$	60.1	116		(Wypych 2008)
MDEA	105-59-9	$C_5H_{13}NO_2$	119.16	245		(DIPPR)
MEA	141-43-5	C_2H_7NO	61.08	171	-	(Wypych 2008)
Piperazine	110-85-0	$C_4H_{10}N_2$	86.14 (anhydr.)	146 (anhydr.)		(Bingham et al. 2001)
Amides						
Acetamide	60-35-5	C_2H_5NO	59.1	222		(Wypych 2008)
Formamide	75-12-7	CH_3NO	45.04	210		(Wypych 2008)
Aldehydes						
Acetaldehyde	75-07-0	C_2H_4O	44.06	21		(Wypych 2008)
Formaldehyde	50-00-0	CH_2O	30.03	-21 (gas)		(Wypych 2008)
Others						
Ammonia	7664-41-7	NH_3	17.03 (anhydrous)	-33 (gas)		(MSDS anhydrous ammonia, 2005)

3. SAMPLE MATRICES

3.1 Matrix 1: Treated flue gas (gaseous)

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

Table 2 Tentative specifications of the treated flue gas

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

n.a. – not available

3.2 Matrix 2: Wash water from the absorber tower (liquid)

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 processes will be present in traces.

3.3 Matrix 3: Reach and lean amine solvent (liquid)

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

Table 3 Examples of aqueous solvents

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

4. ANALYTICAL METHODS

4.1 Analysis of nitrosamines

The analytical methods for N-nitrosamines included in this literature review were mostly developed for ambient air or waste/drinking water. In some cases the matrices were more exotic, like urine, food and cosmetic extracts. The analytical methods for ambient air were considered suitable for flue gas but the differences of these matrices should be taken account already when developing the sampling method. The methods for water suit for wash water but rich/lean amine solvent is more complex. There is no direct mention in the literature of methods developed to quantify traces of nitrosamines in presence of a large amount of alkanolamines or other solvent amines. N-nitrosamines can be divided into volatile (NDEA, NDMA, NMOR and NPIP) and non-volatile (nitrosopiperazine and NDELA) nitrosamines. Almost all the analytical methods for N-nitrosamines involve some kind of chromatographic separation in combination with a detector.

Polarographic and spectrophotometric methods were developed for simple matrices, but they are subjected to interference and have limited application for trace level analysis (OSHA method 27). Thin layer chromatography (TLC) techniques have been used for N-nitrosamines determination. Often they are coupled with derivatization and pre-column or post-column separation. TLC methods are usually simple and inexpensive and can in some case even achieve low limits of detection (LOD). Most commonly, they are only semi-quantitative and have low resolution (OSHA method 17). More sensitive methods are based on denitrosation of nitrosamines and detection of the secondary amines or of the nitrite liberated (Jurado-Sanchez et al. 2007a). Denitrosation is usually carried out with hydrobromic acid – acetic acid – acetic anhydride mixtures. The amine liberated can be detected by fluorescence using dansyl chloride (dansylation), by chemiluminescence using tris(2,2-bipyridyl) ruthenium (III) or by photometry and Griess reaction (Jurado-Sanchez et al. 2007a).

High Performance Liquid Chromatography (HPLC) coupled with a detector has been used for complex mixtures of nitrosamines. The advantage of HPLC is that it can detect both volatile and non-volatile nitrosamines (OSHA method 17). Gas Chromatography with a detector (GC) is the most commonly used technique for analyzing complex mixtures of volatile nitrosamines. Non-volatile nitrosamines are also analyzed with GC after derivatization to volatile compounds. Stainless steel column suit for volatile nitrosamines but glass columns have also been used, though they do not have any particular advantage on stainless steel columns. The most used column packing is 10% Carbowax20 M with 2 % KOH and 80/100 mesh acid washed ChromoSorb W. Capillary and support-coated open-tubular (SCOT) columns give good peak resolutions with N-nitrosamines (OSHA method 17). In general GC is superior to LC for determining volatile amines mostly with respect to resolution, but often also in separation time and sensitivity (Jurado-Sanchez et al. 2009).

Most of the commonly available detectors have been used coupled with GC or HPLC. The Thermal Energy Analyzer (TEA) is the most selective detector for N-nitroso compounds and it is successfully used with both GC and LC (OSHA method 17). Mass spectrometry (MS) is also used in combination to chromatographic methods since it provides a secure way to confirm chemical structure. GC/MS with electron impact or chemical ionization (CI) are used for analysis of volatile and thermally stable nitrosamines (Zhao et al. 2006). Capillary column GC/MS has a detection limit superior to that of GC/TEA. The two methods usually show a good qualitative agreement (Ambrus et al. 2003). GC or LC with tandem mass spectrometry (MS/MS) is one of the most sensitive techniques currently used for the analysis of trace level of N-nitrosamines in water (Kodamatani et al. 2009). Capillary electrophoresis (CE) with UV, fluorescence and MS/MS has also been reported as detection methods for N-nitrosamines in water and tobacco (Zhao et al. 2006). Analysis of complex mixtures of volatile N-nitrosamines are often carried out by GC-TEA or HPLC-TEA using MS for confirmation, while non-volatile N-nitrosamines are analyzed by HPLC-TEA with MS confirmation (Bingham et al. 2001).

Screening methods are intended to classify samples into positive or negative by the presence of N-nitrosamines. The best options for screening methods are direct screening systems, which involve no sample treatment. Full sample treatment for screening methods is justified only if the conventional analytical system is expensive to maintain (Jurado-Sanchez et al. 2007a).

No ASTM standard methods of interest were found for nitrosamines. Two ISO standard methods for the analysis of NDELA in cosmetics are available. ISO 15819:2008 uses HPLC-MS/MS and ISO 10130:2009 uses HPLC, post-column photolysis and derivatization. The methods are applicable only for the detection and quantification of NDELA in cosmetics and raw materials used in cosmetics.

4.1.1 Pre-treatment

Analysis of N-nitrosamines in water at trace level requires extraction and pre-concentration. Liquid-Liquid Extraction (LLE) and Solid-Phase Extraction (SPE) are commonly used. In the case of nitrosamines, SPE is especially suitable due their high polarity and solubility in water. SPE has lower costs and shorter processing time compared to LLE. In addition, SPE can be successfully automatized. LLE requires a large amount of toxic solvents and it is time consuming (Jurado-Sanchez et al. 2007a, Jurado-Sanchez et al. 2009). Solid-Phase Micro Extraction (SPME) can be used instead of SPE to reduce processing time (Grebel et al. 2006).

Amines are usually extracted by weak cation exchangers, since elution is scarce from strong cation exchangers due to the amines basicity (Ambrose et al. 1997). The most common sorbents used in SPE of nitrosamines are Ambersorb 572, RP-C_{18}, active charcoal or the combination of SPE materials like LiChrolut$_{®}$ EN and Ambersorb 572 or Extrelut and Florisil (Jurado-Sanchez et al. 2007a). It was discovered that activated carbon (AC) materials can work as catalysts in the formation of nitrosamines from secondary amines in the presence of oxygen. The phenomenon was observed in surface water and wastewater samples (Padhye et al. 2010). Elution is often performed with solutions containing dichloromethane (DCM).

4.1.2 General considerations on analytical samples

Nitrosamines are susceptible to photodegradation, thus care must be taken not to expose them to sunlight (Goff 1983; OSHA method 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 stable especially if refrigerated. 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. The ThermoSorb/N air sampler for N-nitrosamines has been proved to successfully prevent the in situ formation of nitrosamines. (OSHA method 27)

4.1.3 Specific considerations on some nitrosamines

NDMA is the most researched volatile nitrosamine, since it has been found at trace levels (ng/l) in drinking water and countries are considering limiting legislations against it. NDMA measurements with MS are somewhat limited due to its relatively low molecular weight. Only two ions of NDMA can be used with Electron Impact (EI)-MS. NDMA is relatively volatile and also has a short retention time, which allows it to potentially co-elute with other low molecular weight substances. The use of MS/MS helps overcoming these issues (Richardson 2006). NDMA is also often the volatile nitrosamine with the lowest SPE recovery.

NDELA is a non-volatile nitrosamine often found in cosmetics. Specific analytical methods for NDELA are usually developed for cosmetic samples. Water-soluble cosmetics are often diluted in water prior to analysis, therefore, the analytical methods are considered suitable for water matrices. The UV, refractive index and electrochemical detectors for HPLC are not sensitive for NDELA (Ghassempour et al. 2008).

There is little information about the determination of Dnpz, also a non-volatile nitrosamine. It is suspected that Dnpz forms from piperazine contained in medicines. Therefore, Dnpz is analyzed in biological fluids such as gastric juice and urea (Belal et al. 2000, Walash et al. 2001). With the exception of matrix specific pre-treatments, these methods are considered suitable for water based matrices. Information on N-nitrosopiperazine is extremely scarce. It was analyzed in a mixture of piperazine derivatives for the pharmaceutical industry (Marek et al.1999).

4.1.4 Analytical Methods

Table 4 Analytical methods for N-nitrosamines (Method type: Q=quantitative, S=Screening, G= Group method, total nitroso organic compounds, C= Pre-concentration procedure for aqueous solutions of nitrosamines, MeOH=methanol)

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
vulcanization fumes	NMOR specific	Q		Single ion monitoring SIM-GC/MS Column: RSL Superox FA polyethylene glycol, length 50 m, i.d. 0.32 mm, df 0.3 μm.	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	Extraction with 3:1 mixture of DCM + MeOH	Full Scan GC/MS. GC column: 25 m long by 0.21 mm i.d. Fused silica capillary column coated with Carbowax 20 M to a film thickness of 0.25 μm.	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)
workplace air	Mixture of volatile N-nitrosamines NDMA, NDEA, NMOR, NPIP	S, Q	Extraction with 3:1 mixture of DCM + MeOH	GC/MS Screening GC column: 25-m long by 0.21 –mm i.d. Fused silica capillary column coated with Carbowax 20 M to a film thickness of 0.25 μm.	NDMA and NDEA 0.01 ng, NMOR and NPIP 0.02 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)
workplace air	Mixture of volatile N-nitrosamines NDMA, NDEA, NMOR, NPIP	Q	Extraction with 3:1 mixture of DCM + MeOH	GC/MS/HRMID (High Resolution Multiple-Ion Detection) GC column: 25-m long by 0.21 –mm i.d. Fused silica capillary column coated with Carbowax 20 M to a film thickness of 0.25 μm.	NDMA and NDEA 0.002 ng, NMOR and NPIP 0.004 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, desorption with a solution 1:1 DCM and MeOH	GC-TEA. Column: 10-ft × 1/8-in. stainless steel column containing 10% Carbowax 20M with TPA on 80/100 mesh Chromosorb W AW.	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

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
air	NDMA specific	Q	Collection on two Florisil adsorbent tubes (pre-treated with 11 mg of DL-α-tocopherol) in series, desorption with a solution 1:1 DCM and MeOH	GC-TEA. Column: 12-ft × 1/8-in. stainless steel column containing 10% Carbowax 20M with TPA on 80/100 mesh Chromosorb W AW.	0.4 μg/ m^3, based on recommended air volume.	Average desorption of NDMA was 87.8%. Humidity reduces the adsorption of the amines on the adsorbent.	High maturity: OSHA method 6, Fully Validated
air	Mixtures of volatile nitrosamines in air. NDMA, NDEA, NPIP, NMOR.	Q	Collection by absorption on ThermoSorb/N air samples, desorption with 3:1 mixture of DCM/ MeOH	GC-TEA Column: 10-ft × 1/8-in. stainless steel column containing 10% Carbowax 20M with 2% KOH on 80/100 mesh Chromosorb W AW. Positive GC/TEA results recommended to be confirmed by HPLC/TEA analysis. Column: DuPont Zorbax CN (4.6 mm × 25 cm). Mobile phase: 95% trimethylpentane/ 5% acetone, v/v	.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
air	NMOR specific	Q	Collection by two sampling tubes (Polar Partition and Florisil, both coated with ascorbic acid) connected in series. Desorption by 3:1 (v/v) DCM/MeOH. Light protection, storage in freezer.	GC- TEA. Column: 10-ft × 1/8-in. stainless steel column containing 10% Carbowax 20M with TPA on 80/100 mesh Chromosorb W AW.	0.4 μg/ m^3. Reliable quantitation limit: 0.6 μg/ m^3.	Sensitivity of the analytical procedure (area units per μg/ ml): 44085. Average recovery: 96.3% for treated Florisil tubes and 96.7% for treated Polar Partition tubes. Precision of the analytical method only (pooled coefficients of variation): 0.028.a)	High maturity: OSHA method 17, Fully Validated

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
ambient air	Mixture of volatile nitrosamines NDMA, NDEA, NMOR, NPIP	Q	Collection on Thermo-Sorb/N solid sorbent tube. Elution with 3:1 DCM/MeOH	GC-TEA Column: stainless steel (10 in x 1/8 in) 10 % Carbowax 20 M + 2 % KOH on Chromosorb W-AW.	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)
ambient air	Volatile nitrosamines in industrial ambient air. NDMA, NMOR.	Q	Collection on Thermo-Sorb/N cartridges. Elution twice with 4:1 DCM/MeOH	GC-TEA Column: 25 m capillary column	0.05 µg/ m^3per 100 l of air.		Medium maturity: Article (applicative). (Monarca et al. 2001)
ambient air	Volatile nitrosamines NDMA, NDEA, NMOR.	Q	Collection on Thermo-Sorb/N cartridges preceded by ascorbic acid-impregnated Teflon filters. Elution: 33% MeOH in chloroform, 10 % chloroform in DCM.	GC-TEA Column: capillary DB-Wax 30 m 0.32 mm i.d. 0.25 µm film thickness		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).	GC-TEA. Column: 3 ft x ¼' o.d. 2 mm i.d. glass on column injection, packed with 10 % SP-1000 on 80/100 Supelcoport. The presence of NDELA should be confirmed by HPLC-TEA. Column: DuPont Zorbax CN, 4.6-mm i.d. × 25 cm. Mobile phase: 60 % isooctane, 40 % acetone	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, Fully Validated

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
bulk samples	NDELA specific	S, 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).	Screening by HPLC-UV Column for the reversed phase HPLC/UV work: DuPont Zorbax ODS, 4.6-mm i.d. × 25 cm. Column for the normal phase HPLC/UV work: DuPont Zorbax CN, 4.6-mm i.d. × 25 cm. Reverse phase eluent: 100 % water. Normal phase: 70% isooctane, 20% DCM, 10% MeOH. Quantification by HPLC-TEA: Column: DuPont Zorbax CN, 4.6-mm i.d. × 25 cm. Mobile phase: 60 % isooctane, 40 % acetone GC-TEA: Column: 3 ft x ¼' o.d. 2 mm i.d. glass on column injection, packed with 10 % SP-1000 on 80/100 Supelcoport.	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, Fully Validated
atmospheric samples	Nitroso organic compounds (NOC)	G	Three times extraction by sonication with 1:2 DCM/MeOH	Denitrosation reaction in acid solution with nucleophilic catalyst + nitric oxide analyzed with TEA.	0.8 pmol	Calibration linear dynamic range: 4 orders of magnitude. Linear plot with R=0.9999. Nitrites interfere (decompositon with sulfamic acid (5% wt) in MeOH solution). Rapid (< 5 min) can be used. Excellent selectivity for NOC (only interference nitrates). Water does not interfere. Possibly applicable also to water samples.	Low maturity: Article (Ding et al.1998)

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
environmental water	Hydrophilic organic compounds. NDEA	Q	SPE on activated carbon fiber felt cartridge (KF Type 1500) + extraction cartridge dried by passing air + elution (acetone or DCM).	GC-MS Column: fused-silica bonded with polyethylene glycol J&W DB-WAX, 0.5 µm film thickness, 30m x 0.25 mm i.d.	NDEA 0.02 µg/l	SPE cartridges must be dried to remove water. Overall recovery of NDEA (out of 500 ml water sample with 0.2 µg NDEA) >=84%.	Low maturity: Article (Kawata et al. 2001)
finished drinking water	NDMA, NDEA, NPIP Applicable to nitrosamines that are sufficiently volatile and thermally stable	Q	SPE on cartridge containing 2 g of 80-120 mesh coconut charcoal. Elution with DCM.	GC-MS/MS equipped with a large volume injector and operated in CI mode. CI reagent: MeOH or acetonitrile. Column: capillary columns with medium polarity and low bleed are recommended (Restek Rtx 5SIL MS or equivalent).	NDMA 0.28 ng/l, NDEA0.26 ng/l, NPIP 0.66 ng/l	Interferences: Nitrosamines may be found in rubber products, i.e. also in sample vials with rubber septa. Traces of nitrosamines are commonly present in water. Reagent water must be free of the nitrosamines to be analyzed.	High maturity: US EPA method 521. (Munch & Bassett 2004), article (Richardson 2007)
water	Mixture of nitrosamines NDMA, NDEA, NMOR, NPIP	Q	SPE. Several sorbents. The retention efficiency ca. 100 % with LiChrolut EN and Oasis HLB, on RP-C_{18} and fullerenes it was 53 and 62 %.	GC-electron impact ionization MS. Column: polydimethylsiloxan (95%) cross-linked DB-5 capillary column.	Obtained when using LiChrolut EN for 100 ml sample. NDMA 2.7, NDEA 1.1, NMOR 2.7 and NPIP 1.2 ng/l.	Method for the analysis of different type of amines in water samples in presence of anilines, chloroanilines, and aliphatic amines. Tested on various types of water. Linearity range (ng/l) when using LiChrolut EN for 100 ml sample: NDMA 8-20000, NDEA 3-20000, NMOR 8-20000, NPIP 4-20000. Average recoveries are reported.	Low maturity: Article (Jurado-Sanchez et al. 2009)

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
drinking water	Mixture of nitrosamines NDMA, NDEA, NPIP, NMOR	Q	SPE. The SPE column contained 350 mg of LiChrolut EN (bottom) 500 mg of Ambersorb 572 (middle) and glass wool (top). Elution with DCM.	GC-MS with NH_3 positive chemical ionization (PCI). MSD in PCI mode. Column: J&W Scientific DB-1701 P capillary column, 30.0 m x 0.25 mm i.d. and 0.25 µm film thickness.	NDMA 1.6, NDEA 1.2, NPIP 1.6, NMOR 0.7 ng/l.	Tested on source-water and treated drinking water samples. Recovery of amines from different water samples from SPE cartridges reported. Applications of this method to Alberta (Canada) public drinking water are published by the same authors.	Low maturity: Article (Charrois et al. 2004, Charrois et al. 2007)
drinking water	Mixture of nitrosamines NDMA, NDEA, NMOR, NPIP	Q	Automatic SPE unit using LiChrolut EN. (See above)	GC-MS. DSQ II mass spectrometer. Short capillary column: Supelco Supelcowax-10 capillary column 1.5 m x 0.25 mm i.d. 0.25 µm non-bonded, base modified poly (ethylene glycol).	NDMA 0.05, NDEA 0.02, NMOR 0.08, NPIP 0.03 ng/l	Linear range (ng/l) NDMA 0.2-600, NDEA 0.1-600, NMOR 0.3-600, NPIP 0.1-600	Low maturity: Article (Jurado-Sanchez 2010, Jurado-Sanchez 2007b)
drinking water	Mixture of nitrosamines NDMA, NDEA, NMOR, NPIP	Q	SPE. Resin: Ambersorb 572, Supelco.Optimized amount: 200 mg of resin. Extraction: DCM	GC-MS/MS. Three columns were used: (A) 60 m x 0.32 mm i.d. 1.8 µm film. HP-VOC Agilent Tech. (B) 60 m x 0.32 mm i.d. 1.8 µm film. DB-VRX Agilent Tech. (C) C8 30 m x 0.25 mm i.d. 1 µm film. DB 1701 Agilent Tech. Ion trap MS used either MeOH or acetonitrile as CI reagent.	NDMA 0.78, NDEA 1.78, NMOR 1.38, NPIP 1.35 ng/l	Method validated through round-robin testing (method testing in at least three laboratories in the US and Canada). Concentration Factor (CF) achieved through the extraction procedure: 1250 (from 500 ml to 0.4 ml) Recovery: NDMA 58 % (can be increased by 11% with the addition of NaCl to the extraction eluent), other amines > 80 %.	Medium maturity: Article. Method included in "Standard Methods for the Examination of Water and Wastewater" (New Methods section). (Cheng et al. 2006)

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
drinking water	Mixture of nitrosamines NDMA, NDEA, NMOR, NPIP	Q	CSPE. 5 sorbents. The optimum cartridge was packed with 350 g resin on top (Ambersorb 572, Supelco) and 250 g grafitized non porous carbon (Supelclean ENVI-carb sorbent 57088, Supelco). Elution (problematic) with 6 ml DCM.	GC-MS/MS. Three columns were used: (A) 60 m x 0.32 mm i.d. 1.8 µm film. HP-VOC Agilent Tech. (B) 60 m x 0.32 mm i.d. 1.8 µm film. DB-VRX Agilent Tech. (C) C8 30 m x 0.25 mm i.d. 1 µm film. DB 1701 Agilent Tech.Ion trap MS used either MeOH or acetonitrile as CI reagent.	NDMA 0.7, NDEA 0.84, NMOR 0.63, NPIP 0.33 ng/l	Method validated through round-robin testing (method testing in at least three laboratories in the US and Canada). Concentration Factor (CF) achieved through the extraction procedure: 1000 (from 500 to 0.5 ml). This method is advantageous because it uses large sample volumes, use small solvent amounts and can be run fully automatically.	Low maturity: Article (Cheng et al. 2006)
drinking water	Mixture of nitrosamines NDMA, NDEA, NMOR, NPIP	Q	MLLE 30 g NaCl with 20 ml DCM.	GC-MS/MS. Three columns were used: (A) 60 m x 0.32 mm i.d. 1.8 µm film. HP-VOC Agilent Tech. (B) 60 m x 0.32 mm i.d. 1.8 µm film. DB-VRX Agilent Tech. (C) C8 30 m x 0.25 mm i.d. 1 µm film. DB 1701 Agilent Tech. Ion trap MS used either MeOH or acetonitrile as CI reagent.	NDMA 2.3, NDEA 2.5, NMOR 2.7, NPIP 2.2 ng/l	Method validated through round-robin testing (method testing in at least three laboratories in the US and Canada). Concentration Factor (CF) achieved through the extraction procedure: 200 (from 100 to 0.5 ml). This method achieves higher LOD compared to other traditional LLE extractions but requires less volumes and shorter extraction times.	Low maturity: Article (Cheng et al. 2006)

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
tested on urine and aqueous metal-working fluids	NDELA specific	Q	SPE. Aqueous solutions of metalworking fluids were loaded on an Extrelut 20 extraction cartridge and then extracted with ethyl formate.	GC-TEA derivatization not required in GC-TEA detection. Column: wide-bore polar column AT-WAX 10 m x 0.53 mm, film thickness 1.2 µm from Alltech.	0.3 µg/l.	Ethyl formate contamination can give rise to false positive results up to 1 or 2 µg/l. Linearity range 0-500 µg/l.	Low maturity: Article (Ducos et al. 1999)
aqueous matrices	Mixture of nitrosamines NDMA	Q	Extraction with DCM. The extract is washed with dilute HCl, dried and concentrated to 10 ml or less.	GC-TEA (or GC-NPD) On-column injection Column 1: 1.8 m x 4 mm ID Pyrex glass, packed with Chromosorb W AW (80/100 mesh) coated with Carbowax 20 M/2% KOH equivalent. Column 2: .8 m x 4 mm ID Pyrex glass, packed with Supelcoport (100/120 mesh) coated with 10% SP-2250 or equivalent.	Ppb level. MDL (Method Detection Limit) 0.15 µg/l.	The method was tested for linearity of recovery and it is applicable in the range from 4 MDL to 1000 MDL, where MDL is the method detection limit.	High maturity: EPA method 8070A/ 607(EPA 1996b); (Millar et al. 1984)

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
wastewater	Mixture of nitrosamines NDMA, NDEA, NPIP, (NMOR)	Q	SPME (method developement) Headspace extraction using CAR/PDMS (Carboxen/polydimethylsiloxane) -coated SPME fiber.	GC-NCD (Nitrogen chemiluminescence detection) no NMOR detection GC-NPD (nitrogen-phosphorus detection) no NMOR detection Columns used both for NCD and NPD:(1) Restek DB-1701 30m x 0.32 mm i.d. 1.0 µm film thickness.(2) Supelco Supelcowax 10, 60m x 0.32 mm i.d. and 0.25 µm film thickness. GC-CI-MS (CI MS) Column: Agilent DB-210 capillary column 30m x 0.25 mm i.d. and 0.5 µm film thickness.	LOD (ng/l) for wast ewater. *GC-NCD* NDMA 57, NDEA 87, NPIP 125 *GC-NPD* NDMA 890, NDEA 181, NPIP 1016 *GC-CI-MS* NDMA 30, NDEA 64, NPIP 59, NMOR 138	Total analysis time of 1.25 h. No solvents are needed, extraction and concentration occur simultaneously shortening the time necessary for the procedure. SPME can be automated. The effect of salt and pH on the extraction efficiency of SPME were tested.	Low maturity: Article (Grebel et al. 2006, Grebel & Suffet 2007)
drinking water	Mixture of nitrosamines NDMA, NDEA, NMOR, NPIP (NPYR, NDBA)	SG	Automatic SPE unit using LiChrolut EN.	GC-NPD Short capillary column: Supelco Supelcowax-10 capillary column 1.5 m x 0.25 mm i.d. 0.25 µm non-bonded, base modified poly (ethylene glycol). NPD detector was equipped with rubidium catalyst bed.	NDMA 1.5, NDEA 0.4, NMOR 1.5, NPIP 1.0 ng/l	Gave no false positives during testing. Positive samples were confirmed by GC-MS detection. (see below) Linear range (ng/l) NDMA 5-1500, NDEA 1-1500, NMOR 5-1500, NPIP 3-1500	Low maturity: Article (Jurado-Sanchez 2010); SPE details in (Jurado-Sanchez 2007b)

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
drinking water	Mixture of 9 nitrosamines in water. NDMA, NDEA, NMOR, NPIP	Q	SPE. Automated. SPE on coconut charcoal EPA 521 cartridges. Elution with DCM.	GC/HRMS with isotope dilution. Column: Rtx-5Sil MS 30 m x 0.25 mm i.d., 1 µm film thickness from Restek fused silica capillary column along with a Siltek deactivated splitless liner 3 mm i.d. from Restek.	IDL Instrument LOD (pg) (Resolving power 6000-10000) NDMA 0.43-0.91, NDEA 0.07-0.05, NMOR 1.38-1.30, NPIP 0.07-0.07.	Concentrations of nitrosamines in the test sample were between 302.4 and 730.2 ng/l. Recovery %: NDMA 88 ± 6, NDEA 88 ± 7, NMOR 90 ± 6, NPIP 91 ± 11. Linearity range 1-500 pg.	Medium maturity: Article (Planas et al. 2008); (Munch & Bassett 2004)
aqueous solutions	Mixture of NDEA, NDMA	C	SPE on powdered activated carbon. Elution with DCM	GC-FID Column: 2 m ¼'' o.d. glass column coated with 10 % Carbowax 20M + 2 % KOH on 80-100 mesh Chrom WAW support.	NDEA 1.3, NDMA 3.65 ng/ml	Absorption of NDMA and NDEA from water: 85% and 90%. From beer: 81% and 89%. Lower absorption in presence of alcohol. Recovery from water 96% and 96%, from beer 82% and 90%. Linear range (ng/ml) 10-80 LOQ (ng/ml) NDEA 4.3, NDMA 12.14. Activated Carbon (AC) materials can catalyse transformation of secondary amines to yield trace levels of N-nitrosamines under ambient aerobic conditions. (Padhye et al. 2010)	Low maturity: Article (Ayguen et al.2004)

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
water	N-Nitrosopiperazine (mixture of piperazine derivatives)			GC Column: stainless steel column with diameter 3-4 mm and length 3 m. 5% SE-30 supported on Chromaton N AW DCMS		N-Nitrosopiperazine was not detected on Carbowax 20 M medium-polarity columns.	Low maturity: Article (Marek et al. 1999)
wastewater	Mixture of six nitrosamines NDMA, NDEA, NPIP	Q	SPE with activated charcoal (optimized for NDMA) + elution.	LC-MS/MS Column: 50 mm x 2.1 mm Targa Sprite C18 column (5 µm pore size) equipped with a C18 Guard Column. Mobile phase: MeOH + 2mM ammonium acetate in water.	NDMA: 2 µg/l NDEA: 2 µg/l NPIP: 25 µg/l	Especially for NDMA determination in presence of other nitrosamines. The sample can be injected as an aqueous aliquot. Recovery of NDMA > 98%. Recovery of NDEA was ca. 66 ± 13% and NPIP was ca. 104 ± 8%.	Low maturity: Article (Plumlee et al. 2008b, Plumlee et al. 2008a)
drinking water	Mixture of nitrosamines NDMA, NDEA, NMOR, NPIP. Sensitive both to GC detectable and GC undetectable nitrosamines	Q	SPE Cartridge packed with 350 mg of LiChrolut EN (bottom layer) 500 g of Ambersorb 572 (middle) and glass wool (top). Elution with DCM.	LC-MS/MS (MRM) Column: C_8 capillary column 150 x 0.32 mm i.d., 5 µm). Solvent A: 10 mM ammonium acetate and 0.01 % acetic acid in water. Solvent B: MeOH 100%. Positive EI combined with the multiple-reaction monitoring (MRM).	NDMA: 3.1 NDEA: 10.6 NMOR: 0.2 NPIP: 0.9 ng/l	Recovery from SPE cartridges (%): NDMA: 78 ± 6 NDEA: 93 ± 1 NMOR: 65 ± 7 NPIP: 105 ± 9 Relative response factors (RRFs) estimated.	Low maturity: Article (Zhao et al. 2006, Zhao et al. 2008); Description of SPE: (Charrois et al. 2004)
tested on water soluble samples of cosmetic products	NDELA specific	Q	SPE. C_{18} conditioned Bakerbond column.	HPLC-MS/MS. Column: ChromSep HPLC 150 x 4.6 mm, packed with 5 µm Spherisorb ODS II protected with a guard column. Eluent A: 2 mmol $L^{-1}NH_4Ac$ in water. Eluent B: 2 mmol $L^{-1}NH_4Ac$ in 90% MeOH in water	22.8 µg/kg	SPE mean recovery of NDELA was 88%. Linearity range 0-1600 µg/kg. Limit of quantification 45.6 µg/kg. Uncertainty of the measurements: 17.4 %.	Low maturity: Article (Schothorst & Somers 2005)

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
Matrix non specified.	Mixture of N-nitrosamines NDMA, NDEA	Q	Suitable pre-treatment not specified for desired matrices. Denitrosation with hydrogen bromide + acetic acid. N,N- dimethyl aniline was added to accelerate the reaction (mostly for N-nitrosoaromatic amines). Derivatization into secondary amines in acridone-N-acetyl chloride (ARC-Cl).	HPLC + spectrophotometer Column: 4.6 mm, 5 µm Spherisorb C18. Eluent A: 20 mM ammonium dihydrogenorthophosphate + 9 mM triethylamine-methanol (95:5 %). Eluent B: acetonitrile + water (75:25 n%)	NDMA 24 fmol NDEA 46 fmol	Solvent extraction steps to remove excess derivatization agent prior to chromatography not needed.The derivatives exhibited <4% decomposition. All derivatives gave linear response for peak heights greater than 0.998. Sensitivity depends on column size, narrow or microbore columns give the best sensitivity.	Low maturity: Article, New derivatization agent (You et al. 1999)
water	Mixture of nitrosamines NDMA, NMOR, (DEN)	Q	SPE.	HPLC-UV-chemiluminescense detector (CLD). Column: XBridge C_{18} 250 mm x 4.6 mm i.d., 5µm particle size.Eluent: 10mM borate buffer (pH 10.5) – MeOH (98:2 v/v). UV irradiation time 15 sec. Luminol solution prepared with the addition of carbonate buffer.	NDMA 1.5 ng/l NMOR 2.9 ng/l	Ppt measurements of nitrosamines without pre-concentration step. Tested on samples containing other nitrosamines, nitrites, nitrates and diethylamine. Linear range: 5-1000 ng/l for both NDMA and NMOR.	Low maturity: Article (Kodamatani et al. 2009)

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
drinking water	Mixture of nitrosamines NDMA, NDEA, NMOR, NPIP	Q	SPE using Strata X surface-modified styrene-divinylbenzene polymer. Elution with acetone and air.	HPLC-CLD using two photo-reactors: (1) photo-degradation (2) photo-oxidation with peroxydisulfate Column: Ultrasphere (Beckman) 5 µm C_{18} 250 mm x 4.6 mm. Mobile phase: 5 mM acetate buffer (pH 4) and acetonitrile (95:5 v/v) CL detector: Camspec CL-2 luminometer.	NDMA 0.29, NDEA 0.76, NMOR 0.09, NPIP 0.07 µg/l)	Linear range (µg/l) NDMA 1.5-148, NDEA 4.2-510, NMOR 0.52-93, NPIP 0.36-103. Reproducibility was studied with good results. Recovery of amines from SPE varies form 40 % for NDMA to 90 % for NPIP.	Low maturity: Article (Perez-Ruiz et al. 2005)
tested on water soluble samples of cosmetic products	NDELA specific	Q	SPE. C_{18} Restek.	RP-HPLC-UV detection Column: Eurospher-100 C_{18} 250 mm x 4.6 mm, 5 µm from Knauer. Isocratic elution mode using water, acetonitrile (95/5 v/v). The retention time of NDELA was increased and the shape of the peak improved by adding sodium 1-octanesulfonate (ion complex agent) to the sample before LC.	0.01 µg/ml	Linearity range 0.03-10 µg/ml. SPE average recovery of NDELA was 86.9 %. Limit of quantification 0.03 µg/ml.	Low maturity: Article (Ghassempour et al. 2008)
tested on samples of cosmetic products and biological sample	Mixture of volatile and non-volatile nitrosamines NDELA, NDMA	Q	Pre-treatments reported are suitable for cosmetic products and biological samples.	HPLC-DAD (photodiode array detector). Column: 250 mm x 4.6 mm i.d. Phenomenex Luna CN, particle size 5 µm. Mobile phase: MeOH- 1.0 mM K_2HPO_4.	NDELA 0.02, NDMA 0.02 mg/l	Linearity range 0.2-100 mg/l.	Low maturity: Article (Wang et al. 2006)

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
aqueous solutions	NDELA specific	Q	Extraction with ethyl acetate. Derivatization: alkaline denitrosation of NDELA and reaction of the nitrite liberated with Coumarin 120 (4-methyl-7-aminocoumarin) in sulfuric acid medium to give 7-diazo compounds. Hydrolysis at 100 °C to give 7-hydroxycoumarin. The fluorescent product was extracted with ethyl acetate.	HPLC-fluorimetric detector. Column: 100 mm x 4.6 mm i.d. Spheri-5 cyano-bonded column from Brownee. Isocratic elution with hexane-2-propanol (95:5, v/v).	0.8 µg/l.	Linearity range 1-30 µg/l. Repeatability (R.D.S.) between 6.8 % and 5.5 %. Reproducibility (R.D.S.) 9.2 %.	Low maturity: Article (Diallo et al. 1996)
wastewater	Mixture of 9 nitrosamines in water. NDMA, NDEA, NMOR, NPIP	Q	SPE. Combination of two cartridges: Oasis HLB cartridges (on top) and Bakerbond Carbon cartridges. Elution with DCM.	HPLC-MS Hybrid Linear Ion Trap/Orbitrap MS (LTQ Orbitrap) Reverse-phase column Waters X-Bridge C18, 100 x 2.1 mm, 3 µm particle size with pre-column 10 x 2.1 mm of the same type. Elutions with (A) water and (B) MeOH both containing acetic acid 0.4 % (v/v).	NDMA 0.3, NDEA 0.5, NMOR 0.5, NPIP 0.3 ng/l	Recoveries from SPE in different sample types are given. LOQ (ng/l) NDMA 1.0, NDEA 1.9, NMOR 1.7, NPIP 1.0	Low maturity: Article (Krauss & Hollender 2008)

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
groundwater	Nitrosamines and secondary amines simultaneous determination NDMA, NDEA, NPIP, DEN, DMA	Q	SPE and derivatization. Mini activated carbon column followed by elution with acetone and concentration of extracts by denitrosation and fluorogenic derivatization.	HPLC-CLD Column: reverse-phase C_{18} 83 x 4.6 mm i.d., 3 µm. Mobile phase: acetonitrile-water-ethanol containing imidazole as catalyst and oxalic acid. The chemilumiganic reagent solution contained 2-NPO (bis(2-nitrophenyl) oxalate) and H_2O_2 in acetone-ethyl acetate solvent.	NDMA 4.3, NDEA 4.6, NPIP 5.0, DEN 4.8, DMA 4.8 fmol/l	Recovery ≥ 95 % for all except NDMA (76.3 %). Range of linearity: 0.05-20.00 pmol/l.	Low maturity: Article (Fu & Xu 1995)
tested on beer, tested on smoke	Mixture of N-nitrosamines NMOR, NDMA, NDEA, NPIP	Q	Extraction (different depending on the sample type). Denitrosation with hydrobromic acetic acid. Dansylation with dansyl chloride in a microwave vessel.	HPLC-fluorescence detector. Column: NovaPak C_{18} 4 µm 60 Å (150 x 3.9 mm i.d.) with a Pelliguard LC_{18} guard column. Eluent acetonitrile-water (55:45 v/v)	NMOR 8, NDMA 27, NDEA 75, NPIP 34 pg.	Linearity range (ng/ml) 4.5-75 for NMOR, NDMA and NPIP. 4.5-150 for NDEA.	Low maturity: Article (Cardenes et al. 2002)
tested on simulated gastric juice, pH 1.2- 3.5	Dnpz specific	Q	No suitable pre-treatment is given for wash water.	HPLC-UV. Column: Reverse phase OSD column. Hibar pre-packed column RT 250-4, Lichrosorb RP- 18 (5 µm) combined with guard column. Isoecratic elution with methanol- 0.02 M sodium dihydrogen phosphate.	0.01 µg/ml	Linearity range (µg/ml) 0.072- 2.88. LOQ 0.072 µg/ml. Repeatability, reproducibility and robustness of the method were investigated.	Low maturity: Article (Walash et al. 2001)

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
drinking water	Mixture of nitrosamines NDMA, NDEA, NMOR, NPIP	SG	SPE + derivatization. SPE using LiChrolut EN, elution with ethyl acetate-acetonitrile (9:1) mixture. Denitrosation reagent: hydrobromic acid – acetic acid – acetic anhydride. Derivatization by Griess reagent.	UV/VIS Spectrophotometer.	0.2 µg/l. NMOR 0.3 µg/l	Sorption efficiency on LiChrolut EN close to 100 % for all amines. Reliability and confidence level of 95 %. No false negatives for a cut-off of 0.6 µg/l. Linear range (µg/l) NDMA 0.7-35, NDEA 0.7-40, NMOR 0.9-45, NPIP 0.7-35	Low maturity. Article (Jurado-Sanchez 2007a, Jurado-Sanchez 2007b)
tested in urine	Dnpz specific	Q		Voltametric. Measuring the differential pulse polarographic peak produced in pH 3 Britton Robinson buffer. Three electrode system used: dropping mercury electrode (DME) as working electrode, Ag/AgCl reference electrode and platinum wire auxiliary electrode.	Min. 0.072 µg/ml.	DNPZ is reducible at the DME electrode giving a well defined, diffusion controlled cathodic wave at pH 3 BRb. The relation between the diffusion current and the concentration was found to be rectilinear over the concentration range 0.4-24 µg/ml.	Low maturity: Article (Belal et al. 2000)

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
aqueous solutions	Mixture of nitrosamines NPIP, NDEA	G		Voltametric. Three electrodes: boron-doped diamond (BDD) plate (0.6 cm x 0.6 cm) used as a working electrode, reference system Ag/AgCl (KCl 3.0 mol/l), auxiliary electrode 2 cm^2 Pt foil. Britton Robinson buffer (pH 2).	Min. $6 \cdot 10^{-8}$ mol/l.	Well-defined irreversible oxidation peaks for all N-nitrosamines studied on the BDD electrode. The difference between the peak potentials of the nitrosamines was only 10mV, therefore the method is suitable only for group determination. Reasonable linearity of current vs. concentration in the range $2 \cdot 10^{-6}$ – $1.36 \cdot 10^{-5}$. QL $2 \cdot 10^{-7}$ mol/l	Low maturity: Article (Soares de Oliveira et al. 2008)
tested on food, drinks, biological fluids, cosmetics	N-nitroso compounds	G	Treatment with sulfamic acid (SA). Denitrosation with CuCl in HCl.	Chemiluminescence. Nitric Oxide Analyzer (NOA 280) equipped with a Radical Purger Reaction Vessel from Sievers Inc.	Tested with NPRO (nitrosoproline) 1 pmol	Linearity: 4 pmol -2 nmol (NPRO). A commercially available one-piece reaction vessel and NO analyzer used (NO release rapid). CuCl was suitable for samples in aqueous and most organic solvents (except CH_2Cl_2, $CHCl_3$). Interferences: Nitrates, minimized by anion-exchange resins treatment. Nitrite, O-nitroso, C-nitroso, C-nitro and other organic nitrogen compounds: interference eliminated by SA. S-nitroso compounds may interfere with the analysis.	Low maturity: Article (Wang et al. 2005)

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
pool water	N-nitrosamines	G	Liquid-liquid extraction with ethyl acetate. Denitrosation with a reduction solution containing 13.5 mL glacial acetic acid and 1 mL of an aqueous 540 g/L iodide and 114 g/L iodine.	Chemiluminescence.	NDMA 5 ng/l.	Interfering species: nitrite and S-nitrosothiols. Eliminated by pre-treating the samples (described). Average extraction efficiency: 56 %. Range of linearity. 100 nM-100 µM. as NDMA.	Low maturity: Article (Kulshrestha et al. 2010)
drinking water	Mixture of volatile nitrosamines NDEA, NPIP	Q		Capillary Electrospray -FAIMS-MS/MS. Capillary Electrospray - High-Field Asymmetric waveform ion mobility spectrometry (FAIMS).	NDEA and NPIP 5ng/l	Linearity range (ng/ml) NDEA 20-1000, NPIP 10-1000.	Low maturity: Article (Liu et al. 2007)
aqueous synthetic samples	Mixture of nitrosamines NDMA, NMOR, NPIP	Q	Direct application to aqueous samples. (Tested only on synthetic water samples.) SPE can be used as concentration method.	MEKC. Micellar Electrokinetic Capillary Chromatography on a fused-silica capillary. The running electrolyte was phosphate-borate solution.	NDMA 0.16, NMOR 0.24, NPIP 0.21 mg/l	Linearity range (mg/l) 0.25-10. QL (mg/l) NDMA 0.52, NMOR 0.82, NPIP 0.71	Low maturity: Article (Sanches Filho et al. 2003)

a)The precursors of NMOR (morpholine, and nitrosating agents such as oxides of nitrogen, nitrites, etc.), are possibly present in the environment. It is therefore conceivable that NMOR may be formed upon the sampling device and not be present in the sampled air. Laboratory experiments indicate that it is possible to form NMOR from its precursors on an untreated air sampler. Further experiments show that when the tubes are treated with 10 mg of L-(+)-ascorbic acid, the formation of NMOR does not take place.

4.2 Analysis of alkylamines

As in the case of nitrosamines, most of the analytical methods for alkylamines presented in this report were developed for air or water matrices. Alkylamines are usually present as trace amounts. The analytical methods for air were considered to be applicable for flue gas while the methods for water should be suitable for wash water. Rich/lean amine solvent is equally problematic as in the case of nitrosamines, since any analytical method developed to quantify alkylamines as trace compounds from an aqueous solution of alkanolamines was not found. Analytical methods that simultaneously detect alkylamines and alkanolamines are available in the literature. However, these methods are suitable for wash water, where both alkanolamines and alkylamines are present as trace compounds.

Low molecular weight (LMW) aliphatic amines are precursors to carcinogenic nitrosamines via nitrosation (Lamba et al. 2008). GC coupled with MS or FID (Flame Ionization Detector) detectors are the most commonly used instruments for the determination of LMW aliphatic amines. GC/MS has been recognized as the method of choice for the analysis of aliphatic amines in environmental samples, due to its superiority in selectivity and sensitivity (Akyuez & Ata 2006). The determination of LMW amines by GC presents challenges due to their aqueous solubility, volatility, polarity and basicity (Namiesnik et al. 2003). In particular, their dipole moment leads to strong sorption giving rise to tailing peaks, ghosting phenomenon and low sensitivity (Lamba et al. 2008). Primary amines have the strongest sorption tendency, followed by secondary amines and tertiary amines. MMA and DMA are the most difficult amines to detect directly by GC (Namiesnik et al. 2003). Primary, secondary and tertiary alkylamines have been analyzed without derivatization by GC/FID (Namiesnik et al. 2003). To overcome the difficulties connected to direct GC analysis, LMW primary and secondary aliphatic amines are often derivatized prior the analysis (Lamba et al. 2008). Many derivatization agents are used, e.g. phthalaldehyde (OPA), dansyl chloride (Dns-Cl), 9-fluorenylmethyl chloroformate (FMOC), fluorescamine (fluram), N-hydroxysuccinimidyl fluorescein-O-acetate (SIFA), 1-nahthylisothiocynate, 4-fluoro-7-nitrobeno-2-oxa-1,3-diazole (NBD-F) and phenylisothiocynate (Lamba et al. 2008). Tertiary amines do not react with derivatization agents (Rampfl et al. 2008), therefore they are analyzed either directly by GC (OSHA method PV2060, Namiesnik et al. 2003) or by HPLC (Rampfl et al. 2008, Claeson et al. 2004). These methods were mostly developed for air matrices; the information on the analysis of tertiary alkylamines in water matrices is scarce. GC/NPD methods were also found (Maris et al. 1999; Abalos et al. 1999).

LMW aliphatic amines are analyzed also by HPLC often coupled to pre-column derivatization. HPLC has been used with either ultraviolet (UV) or fluorescence (FL) detectors (Fournier et al. 2008). For complex matrices, mass spectrometry is preferred for the confirmation of the different amines also in the case of HPLC (Fournier et al. 2008). Other analytical methods reported for LMW aliphatic amines are spectrofluorimetry, capillary electrophoresis (CE) and capillary electrochromatography. Electrochemical detection methods, such as amperometry and potentionetry, are gaining importance due to their low cost and simple instrumentation (Lamba et al. 2008). Neither ISO nor ASTM standard methods of interest were found for LMW alkylamines.

4.2.1 Pre-treatment

In the analysis of trace level of LMW alkylamines, the sample often undergoes several extraction and sample enrichment steps in order to achieve a good recovery of the analyte. Commonly, the sample enrichment techniques are LLE, SPE and more recently SPME (Meseguer Lloret et al. 2002). The extraction step can be performed either before or after the derivatization. Sometimes the concentration step is combined with the derivatization step, e.g. on SPE cartridges, in the quest of reaching lower limits of detections. For HPLC, SPE was proven to be more efficient than LLE (Meseguer Lloret et al. 2002).

Usually LMW amines are extracted with SPE using CG-120 resin or cation exchange sorbents, while the products of derivatization are extracted with C_{18} sorbents (Meseguer Lloret et al. 2002). The extraction with SPE of derivatives from a solution prior to HPLC can lift the HPLC method to the level of detection of GC/MS methods using more affordable instrumentations (Meseguer Lloret et al. 2002). SPME has emerged in recent years as an attractive alternative to conventional extraction method both coupled to GC and LC (Herraez-Hernandez et al. 2006).

Table 5 Analytical methods for alkylamines (Method type: Q=quantitative, S=Screening, M= Monitoring, MeOH=methanol)

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
air	MMA, DMA, EA, DEN and other aliphatic and aromatic amines.	Q	Pre-concentration by percolating the air samples through an acidic solution, ion-pair extraction with bis-2-ethylhexylphosphate (BEHPA), derivatization with isobutyl chloroformate (IBCF).	GC-MS Column: ZB-5 ms, 30 m, I.D.: 0.25 mm, 0.25µm.	0.08-0.01 ng/m^3	Recovery 75.6 – 96.8 %,	Low maturity: Article (Akyuez 2007)
air	MMA, DEN, and other primary/ secondary aliphatic amines.	Q	Derivatization with polymeric resin containing a (pentafluorobenzoyl) PFB group (synthesized). Derivatization products are pentafluorobenzamides.	GC-MS Column: DB-5 ((30mx0.35 mm, i.d. 1.0 µm)	2 pg/2µl	Linearity range 5-250 µg/ml R=0.9956	Low maturity: Article (Jedrzejczak & Gaind 1993)
air	TMA, TEA, specific.	Q	Sampling onto XAD-7 resin coated with 10 % phosphoric acid. Desorption with 1:1 MeOH: deionized water solution. Dilution in 1.0 N NaOH: MeOH solution.	GC-FID Column: Stabilwax DB(60mx0.32mm, 1.0 µm)	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 no. PV2060
air	MMA, EA, DMA, DEN, TMA, TEA	Q	SPME on 65 µm polydimethylsiloxane/ divinylbenzene coating (Supelco)	GC-FID Column: Stabilwax-DB/KOH megabore column (60 m x 0.53 mm x 1.5 µm)	MMA 0.31, EA 0.38, DMA 0.67, DEN 0.21, TMA 0.19, TEA 0.3 LOQ (mg/m^3): MMA 1.03, EA 1.06, DMA 1.88, DEN 0.57, TMA 0.55, TEA 0.86 mg/m^3	The linearity of the method was investigated for each amine.	Low maturity: Article (Namiesnik et al. 2003)

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
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).	GC-FID Column: 1.8m x 4 mm ID glass, 4 % Carbowax 20M+ 0.8% KOH on Carbosieve B (60/80 mesh)	0.02 mg/sample	Range of applicability (20 l air sample): 25-550 mg/m^3 DEN, 7.5-130 mg/m^3 DMA. Overall accuracy 18.7 % 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 increase sensitivity.	High maturity: NIOSH method 2010 (NIOSH 1994d)
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.	HPLC-MS/MS Column: Grom-sil 80 ODS-7, 4 μm, 200 x 3 mm.	0.12-0.25 ng/μl	The linearity varied between r^2=0.997 and r^2=0.999. Additional sensitivity can be achieved by using a micro-column.	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.	HPLC-MS/MS Column: Supelco HSF5 3μm particle size, 150 x 2.1 mm.	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.	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)

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	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). The products of dansylation are fluorescent aromatic sulfonamides.	HPLC/ESI-MS Electrospray Ionization (ESI). Column: Phenomenex Luna C_{18} (3 μm, 150 x 2.0 mm). Mobile phase: Acetonitrile + 1% formic acid and water.	LOQ (external calibration): DEA 0.09, MEA 0.05, MMA 0.02, DMA 0.07 μg/ml	Sensitivity with external calibration (ml/μg): DEA $1.5\cdot10^7$, MEA $1.7\cdot10^7$, MMA $3.4\cdot10^7$, DMA $4.2\cdot10^7$ 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	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).	HPLC-fluorescence or visible (VIS) detector. Column: Waters radial CN column. Mobile phase: isooctane : isopropanol (80:20)	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,	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
air	DMA Specific	Q	Sampling onto XAD-7 resin coated with 10 % (w) NBD chloride. Desorption with tetrahydrofuran (small amount of bicarbonate present).	HPLC-fluorescence or visible (VIS) detector. Column: Waters radial CN column. Mobile phase: isooctane:isopropanol (80:20)	LOD and Reliable quantitation limit: 24 ppb (43 μg/m^3) DMA,	Standard error of estimate at the target concentration: 5.5 % DMA, Recovery %: DMA>93	High maturity: Fully validated OSHA method 34

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
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.	On-line solid phase derivatization-HPLC-UV/FL On-line pre-column derivatization and reverse phase HPLC-UV/FL. Column: EM Science LiChrospher C_{18}, 5 μm 250 x 4.6 mm i.d. UV-VIS detector. Pre-columns: Stainless steel 27 x 2 mm i.d.	24 ppb MMA, 60 ppb DEN	Recovery MMA 95.6%, DMA 90.3%, DEN 91.0%. Percent of derivatization: 88 % for primary amines and 75 % for DEN. Range of validation: 15-47 ppm. Quantitations from 0.02 to 0.38 mg/m^3 air.	Low maturity: Article (Gao et al. 1990)
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).	Semi-quantitative estimation of the amine by visual inspection of the cartridges Quantitative test performed with spectrophotometer	DMA 2, (MMA 9, EA 17-21, DEN 11-10 μg^{-1}	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 2004)

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
aqueous samples; emissions in a compost treatment plant	MMA, EA, DMA, DEN, TMA, TEA, and other C_1-C_4 aliphatic amines	Q	Concentration with a mixture of salts (NaCl and K_2SO_4). This technique has been applied for the monitoring of amine concentration at sub-µg/m^3 level in compost treatment plant (absorption samples in an HCl solution).	Head-space-GC-NPD Column: PoraPLOT Amines capillary column, 10 µm, 27.5m (with 2.5m particle trap) x 0.32mm	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 %	Low maturity: Article (Maris et al. 1999)
wastewater, river water, sea water and sediment	MMA, DMA, EA, DEN, and other aliphatic and aromatic amines	Q	Extraction with chloroform and chloroform + BEHPA (bis-2-ethylhexylphosphate), derivatization with isobutyl chloroformate (IBCF).	GC-MS Column: ZB-5 ms, 30 m, I.D.: 0.25 mm, 0.25 µm Both EI and positive and negative ion chemical ionization (PNICI) modes used.	MMA 0.5, DMA 0.44, EA 0.39, DEN 0.3 ng/l	Recovery % at optimum extraction pHs: MMA 81, DMA 87, EA 90, DEN 92 Recovery % at pH 8: MMA 76, DMA 87, EA 90, DEN 91	Low maturity: Article (Akyuez & Ata 2006)
surface water and waste water	Piperazine. Aliphatic and alicyclic amines- > C_3 may be possible also for < C_3	Q	2 different methods. Sample preparation schemes (enrichment and derivatization) are described in the article. In the GC/MS-method the derivatization is done with tricloroethyl chloroformate (TCECF) and in the HPLC-method with 9-fluorenylmethyl chloroformate.	(1) GC/MS column: DB-5 fused silica capillary column (30 x 0.25 mm, 1 µm film thickness) (2) HPLC-FL Column Macherey-Nagel ET- (150 mm/ 4 mm/ 8 mm Nucleosil packed with 5 µm C18 material). Eluent: acetonitrile in water.	(1) GC-MS: 0.15 µg/l for C_3 (2) HPLC: 0.03 µg/l for piperazine	(1) RSD: 7.5 % R^2= 0.9967 for C_3 (2) RSD: 1.7 % R^2= 0.9999 for piperazine.	Low maturity: Article (Pietsch et al. 1996)

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
environmental waters	Aliphatic and aromatic amines, not suitable for tertiary amines. Ammonia.	Q	Derivatization with benzoyl chloride. SPE of the derivatives.	GC-MS Column: HP-5 ms capillary column, 30 m, I.D.: 0.25 mm, 0.25μm film thickness.	7- 39 ng/l, Ammonia 20 µg/l.	RSD 2.8-22.3 %. Linear range: 0.1-100 µg/l.	Low maturity: Article (Mishra et al. 2001)
sample matrix not given	MMA, EA and other primary and secondary aliphatic amines	Q	Derivatization with N-hydroxysuccinimidyl phenylacetate (SIPA), separation of the organic phase, wash and evaporation to dryness and dissolution into DCM	GC/MS (EI mode) and GC/FID (analytical calibration). Column: OV-1701 (25 m x 0.2 mm i.d., 0.11μm film thickness)	MMA 0.7, EA 1 pmol / FID.	RSD %, 1.9 MMA, 2.7 EA. Linearity R^2= 0.9977 MMA, 0.9992 EA. The derivatives very stable.	Low maturity: Article (Zhao et al. 2002)
tap and river water	EA, Aliphatic amines and other volatile organic compounds	Q	Micro-extraction into a single drop using as solvent benzyl alcohol containing 2-butanone as an internal standard.	GC/FID Column: CP-Cil 5 (10m x 0.25mm, 0.12 μm)	EA 25 μg/l	RSD 12 %, R^2= 0.9130	Low maturity: Article (Kaykhaii et al. 2005)
waste water and sewage-polluted water	MMA, DMA, TMA, DEN, TEA, (C_1-C_6 free volatile amines)	Q	Acidification with HCl to pH 1-2. Headspace sampling using SPME with polydimethylsiloxane (PDMS) coating.	GC-NPD Column: PoraPLOT amines (30m x 0.32 mm i.d., 10 μm film thickness)	MMA 27, DMA 21, TMA 11, DEN 3, TEA 14 μg/l	RSD 13-33% Linearity range: MMA 32-686, DMA 20-608, TMA 47-563, DEN 52-611, TEA 60-714.	Low maturity: Article (Abalos et al.1999)

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
sample matrix not given	MMA, EA, and other aliphatic amines	Q	Derivatization in pre-column with N-hydroxysuccinimidyl fluorescein-O-acetate (SIFA)	LC-UV/VIS Column: C_{18} (5 μm, 250 x4.6 mm) Mobile phase: MeOH + water – citric acid-Na_2HPO_4 buffer.	MMA 163, EA 247 amol	SIFA has high fluorescence quantum yield in the visible region, it is specific to aliphatic amines, needs mild derivatization conditions and gives origin to few by-products. Linearity range (pmol): MMA 0.0001-4, EA 0.003-4	Low maturity: Article (Wang et al. 2000)
sample matrix not given	MMA, EA and other C_1-C_7 aliphatic monoamines	Q		LC-UV, stationary phase unfunctionized polymethacrylate resin (TSKgel G3000PW_{XL} 150 mm x 6 mm i.d.) with 10mM sodium hydroxide containing 0.5 mM C_8 amine (1-methylheptylamine) at pH 11.9 as the eluent.	MMA 11 μM, EA 4.5 μM	RSD 1.1 % for peak areas	Low maturity: Article (Ohta et al. 2004)
tap and river water	EA, DMA, and other aliphatic amines	Q	Pre-concentration and pre-column derivatization on solid-phase extraction SPE cartridges Bond Elut C_{18}. Derivatization agent 3,5-dinitrobenzoyl chloride (DNB). Elution with acetonitrile.	LC-UV Column: Hypersil ODS C_{18} (250 x 4.6 mm, 5 μm film thickness). Mobile phase: acetonitrile – water.	DMA 2, EA 5 μg/l	Unreacted DNB did not interfere in the chromatography. Recovery after pre-concentration and derivatization: EA 77 %, DMA 81 %. Linearity investigated in the concentration range 0.050-1.0 mg/l (r^2): DMA 0.991, EA 0.99.	Low maturity: Article (Verdu-Andres et al. 2001)

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
flotation liquors	Aliphatic amines C_6-C_{18} may possible also < C_6	Q	Sample pre-treatment (conditioning and filtration, etc.) for flotation liquors is explained in the article. Derivatization with 4-cloro-7-nitrobenzofuran.	HPLC-UV/VIS Column: Nova-Pak C_{18}, 150 mm x 3.9 mm i.d. Several mobile phases were used.	dodecylamine 10 ppb	Straight-line calibration curves were obtained up to at least 200 ppm of amine solution. Linearity range (tested with dodecylamine): 0.0025 mM to 1.0 mM. No interfering substances were found.	Low maturity: Article (Hao et al. 2004)
lake water and industrial wastewater	MMA, EA, DMA, DEN, Low molecular weight aliphatic amines. Tested on 7 amines and ammonium.	S	Concentration and derivatization on Bond Elut C_{18}-SPE cartridges (200 mg). Derivatization agent: dansyl chloride (dansylation). Elution with acetonitrile.	HPLC-UV or FL Column: C_{18} LiChrospher 125 x 4 mm i.d. 5 µm film thickness. Mobile phase: acetonitrile – imidazole (pH 7).	MMA 2, EA 2, DMA 3, DEN 4 µg/l (FL detector). MMA 3, EA 6, DMA 6, DEN 15 µg/l (UV detector). For sample volumes 5 ml and elution volume 0.5 ml. The LOD decreases while working with smaller water samples.	Linearity: $r^2 > 0.99$ for all amines. The recovery values form SPE cartridges are low (lower than 75 %) in real water samples for MMA and EA. DMA and DEN showed better recovery (> 75 %).	Low maturity: Article (Meseguer Lloret et al.2002)

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
tap, river and waste water	MMA, DMA, TMA and also possible for other short-chain aliphatic amines	Q	Concentration and derivatization using SPME. Three different schemes were tested: (1) Derivatization in solution and derivatives extraction with SPME. (2) Extraction of amines on SPME and derivatization in solution (3) Simultaneous derivatization and extraction on SPME support. Derivatization agent: FMOC (9-fluorenylmethyl chloroformate). SPME support: Carbowax-templated resins (CW-TR, 50 µm, Supleco). Option (3) was the best option, especially with respect to sensitivity.	HPLC-FCD Column: LiChrospher 100 RP_{18} (125 mm x 4 mm I.D.) Mobile phase ACN-H_2O + pre column for SPME: 20 mm x 2.1 mm i.d. dry-packed with Hypersil C18 30 µm stationary phase.	5 ng/ml for MMA and DMA, 250 ng/ml for TMA	Linearity R^2=0.98 in the concentration interval 0.1 – 1.0 µg/ml for MMA and DMA, concentration interval 1 – 10 µg/ml for TMA. Repeatability (n=3) MMA 2%, DMA 12%, TMA 16% (intraday precision).	Low maturity: Article (Herraez-Low maturity: Hernandez et al. 2006)
lake water	MMA, EA, MEA, DMA. Primary and secondary aliphatic amines and alkanolamines.	Q	Derivatization with N-hydroxysuccinimidyl 4,3,2´-naphthapyrone-4-acetate.	Reversed-phase-HPLC with spectrofluorimetric detection. Column: Lichrosorb $RP\text{-}C_8$ 250 x 4.6 mm i.d. 10 µm, Merck.	MMA 2.4, EA 5.1, MEA 2.1, DMA 16 fmol/20 µl injection.	The presence of salt and other organic substances in the water samples does not interfere with the analytical method. Linearity range (µmol/l): 0.01 – 1.0. Linearity r^2: MMA 0.9999, EA 0.9995, MEA 0.9990, DMA 0.9972.	Low maturity: Article (Liu et al. 2001)

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
red wine	MMA, EA and other primary biogenic amines	Q	SPE described for wine. Derivatization performed on-column. Derivatization agent: o-phthalaldehyde pumped along with the mobile phase.	On-column derivatization HPLC-fluorometric detection. Column: Asahipack OP-50, 5µm, 250x4.6 mm. Three elution solutions used as mobile phase.	100-300 µg/l	Quantification limit was 0.5 mg/l. The reproducibility and repeatability are studied. Linearity range: 0.5-15 mg/l	Low maturity: Article (Busto et al. 1997)
water	DMA, DEN, and secondary aliphatic amines also alkanolamine DEA	Q	Pre-treatment, depending on the amine matrix, explained. Derivatization with 5-isothiocyanato-1,3-dioxo-2-p-tolyl-2,3-dihydro-1H-benz[de]isoquinoline (MCPBA), followed by oxidation with 3-chlorobenzoic acid to form corresponding formamidines.	HPLC-fluorescence detector Column Lichrospher RP-18 (300 x 4 mm, 5 µm particles).	200-300 fmol (20 µl injected)	The samples were stable in brown glass vials. The stability of the derivatives (formamidines) was about 1 h. The detector signal was linear for all formamidines tested over the range from 0.5 to 20pmol (>0.997).	Low maturity: Article (Khalaf & Steinert 1996)
water, human urine, serum	EDA, MMA, EA. Aliphatic primary amines and diamines.	Q	Water was filtered prior to derivatization. Pre-column derivatization with 2, 6-dimethyl-4-quinolinecarboxylic acid N-hydroxysuccimide ester (DMQC-OSu).	HPLC-FL Reverse phase chromatography. Column: 150 x 4.6 mm i.d. 5 µm particle Eclipse XDB-C_{18} column. Eluent: contained water and MeOH	MMA 0.02, EA 0.02, EDA 0.02 nmol/l Reliable real water sample quantification in the range 0.07-4 nmol/l.	Linearity range: 1-80 (nmol/l). R^2 = 0.9999 for MMA and EA, 0.9994 for EDA. Interferences: DMQC-OSu reacts with amino acids but do not interfere with the chromatography analysis. No interferences from alcohols were found.	Low maturity: Article (Huang et al. 2009)

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
lake water	Low molecular weight aliphatic amines. Tested on mixtures of 5 amines.	Q	Samples acidified with HCl and filtered, derivatization with naphthalene-2,3-dicarboxaldehyde (NDA).	HPLC-amperometric detection Column: supelcosil ABZ PLUS (5µm, 100 x 2.1 mm) Mobile phase: MeOH–water (80 : 20 v/v).	23.3-34.4 nmol/l	Recovery: 52.2-127.9%, RSD in peak areas < 5.8%	Low maturity: Article (Lamba et al. 2008)
plant tissue	MMA, EA, DMA, alkanolamine MEA, ammonia and other amines	S	Suitable pre-treatment not specified for desired matrices. Derivatization with dansyl chloride with amines in aqueous solution.	HPLC-UV/VIS Column: Brownlee Spheri-5 RP-18 C_{18} (5µm, 250x4.6mm).	LOD varied with the relative intensities, generally of 5 – 10 pmol.	Linear in range of 2 -16 µM for all the other amine except ammonia, MMA and DMA.	Low maturity: Article (Price et al. 1992)
residual water, river water and human urine	MMA, EA, DMA, DEN, TMA, TEA and alkanolamines EDA, MEA. Ammonia and other aliphatic amines	M	Samples are filtered and reagent solution m-nitrobenzene is added.	Spectrofotometer	MMA 0.5, EA 1.0 DMA 1.0, DEN 0.5, TMA 0.5, TEA 2.0 EDA 1.0, MEA 1.0 mg/l	Maximum concentration detected (mg/l): MMA 10, EA 6 DMA 6, DEN 8, TMA 10, TEA 8 EDA 6, MEA 5	Low maturity: Article (Siddiqi & Pathania 2003)

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
tap and river water	Aliphatic amines > C_3 may be possible also for < C_3	Q	Cleanup and pre-concentration of samples was made in minicolumns (2.5cm x 1.6mm), packed with C18, eluation of samples with 50 nM HCl in 90:10 water-MeOH, adjusted to pH 11 with NH_3	pCEC-MS (pressure assisted chromatography with MS detection) Electrophoretic capillary: monolithic silica electrochromatographic column (30cm x 50µm, back pressure 8 bar) bonded with monolithic octadecyl fused-silica capillary (30 cm) (ODS, Merck).	2-4 µg/l	CEC, capillary electrochromatography, is a hybrid technique between capillary electrophoresis and capillary HPLC. RSD 2.6-4.2 %, recovery 97-106 % R^2 = 0.993-0.998	Low maturity: Article (Santos et al. 2004)
aquarium and river water	MMA, EA, DEN, alkanolamine MEA, ammonia and other aliphatic amines.	Q	Centrifugation on filtration to remove solids. Derivatization with 4-chloro-7-nitrobenzo-2-oxa-1,3-diazole (NBD-Cl)	MEKC-LIF (micellar elektrokinetic chromatography with laser induced fluorescence detection) Column: fused-silica 57 cm (50 cm to the detector) x 75mm	MMA 0.2 MEA 0.1 EA 0.1 DEN 0.1 ng/ml	The signal response was linear over three-order of concentrations (r^2 > 0.99) Range (µg/l): MMA 0.03-6 MEA 0.01-6.0 EA 0.015-6 DEN 0.01-12 Recovery: 90.2 – 110.8 % RSD for peak area: 1.76-2.01 % LOQ (ng/ml): MMA 0.7 MEA 0.3 EA 0.3 DEN 0.3	Low maturity: Article (Hui et al. 2010)

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
biological samples	MMA, EA and other aliphatic amines	Q	Sample in chloroform, derivatization with N-hydroxysuccinimidyl fluorescein-O-acetate (SIFA)	CE-laser-induced fluorescence detector (LIF) Column: uncoated fused-silica (60.2 cm, 50cm to the detector, 75 μm I.D.)	MMA 0.02-EA 0.1 nM	RSD 1.01-4.26 % for peak area. Linearity: MMA range 0.002 – 2 µm, R^2= 0.9995, EA range 0.002 – 1 µm, R^2= 0. 9985	Low maturity: Article (Deng et al. 2009)
pharmaceuticals substances	Method optimized for hydroxylamine. MMA, EA, MEA, DEA. Small amines: alkylamines and alkanolamines + other amines and ammonium.	Q		Capillary Ion Electrophoresis (CIE) with direct conductivity detection. ConCap^{TM} I fused silica capillaries, 50 µm i.d. x 375 µm o.d. x 60 cm. Buffer: 30 mM MES – 30 mM glycylglycine.	1 ppm (given only for hydroxylamine).	Linearity range: 0.05 – 0.5 mM, r^2 > 0.99	Low maturity: Article (Bowman et al. 2000)

4.3 Analysis of solvent amines

Amines, mostly alkanolamines, are used in the oil industry to remove H_2S and CO_2 from post-refining gases. In the literature analytical methods developed to quantify the concentrations of solvent amines in process fluids similar to rich/lean amine solvent, i.e. amines amount well above trace level, were found. Acid-base titration in the presence of an indicator or potentiometric titration using a glass electrode are two methods traditionally employed in the industry to analyze the amount of solvent amines in the circulating water + amine solutions of gas sweetening units. The results of these methods may be erroneous when the degree of degradation of the amines is considerable and when other amines or ammonium ions are present (Kaminski et al. 2002). These traditional methods are not accurate enough for trace determination of alkanolamines but they might be used as quick group methods for the determination of the total amount of amines.

The analytical methods presented in this section were developed for the trace determination of alkanolamines in flue gas (methods for air) or in wash water (methods for water) as polluting agents. Methods for the quantitative determination of alkanolamines and the products of their degeneration in aqueous alkanolamine solutions from gas sweetening units were also included, since they suit rich/lean amine solvent. The use of alkanolamine systems for the removal of carbon dioxide from large point sources, such as power plants, is relatively new and therefore the available published literature is limited. Some aspects of the analysis of rich/lean amine solvent are discussed in (Supap et al. 2006, Strazisar et al. 2003).

Alkanolamines are very water soluble; therefore their analysis presented challenges especially at trace level (Headley et al. 2002). Alkanolamines are highly polar and therefore difficult to separate chromatographically when in a mixture (Worsfold& Yan 1991). Many of the analytical procedures for an individual alkanolamine are applicable or adaptable to a wider range of alkanolamines (Headley et al. 2002). Alkanolamines are analyzed with GC or, even more frequently, with LC using a variety of detectors. Sometimes an extraction/concentration step is required prior to chromatography, especially in the case of GC. Traditionally LLE with organic solvents, water or a combination of these was used as the main sample preparation technique (Headley et al. 2002). Derivatization is sometimes used to improve the chromatographic separation of alkanolamines (Headley et al. 2002), especially if GC is used. GC is usually combined to FID or MS detectors. Liquid chromatography is often preferred to GC in the analysis of alkanolamines because such a methods can be developed that need neither sample preparation nor derivatization. In fact, reverse phase LC, as well as Ion Chromatography (IC), is compatible for aqueous samples and polar water-soluble solutions. The detectors used with LC are UV, chemiluminescence, spectrometric, conductivity or pulsed amperometric detectors (Headley et al. 2002, Dobberpuhl & Johnson 1995).

Ion Chromatography (IC) and Capillary Ion Electrophoresis (CIE) are also reported for the simultaneous determination of amines, alkanolamines and alkylamines, in water samples. CIE permits more efficient separation in less time and with a much lower consumption of the mobile phase with respect to IC. With CIE cations and ions are determined within the same run. On the other end, IC has greater reproducibility of migration time and accuracy compared to CIE (Bowman et al. 2000).

No suitable ISO standard methods were found for solvent amines. ASTM D7599 – 09 is a standard test method for the determination of diethanolamine, triethanolamine, n-methyldiethanolamine and n-ethyldiethanolamine in water by single reaction monitoring LC-MS/MS.

Table 6 Analytical methods for solvent amines (Method type: Q=quantitative, S=Screening, M= Monitoring, MeOH=methanol).

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
ambient air	MEA	Q	Sampling on tubes containing XAD-4 resin coated with cyclohexanone as derivatization agent. Desorption with MeOH.	GC-TSD (Thermionic (nitrogen-phosphorous Specific Detector). Column: DB-Wax megabore silica fused column, 15 m x 0.53 mm i.d., 1.0 µm film thickness.	1µg	Cyclohexanone gives stable derivatives and TSD allows GC in presence of excess reagent. Collected samples were stable for at least 2 weeks. Working range: 0.5 – 20 mg/m^3 in a 10 l air sample. Recovery of MEA from the tubes: between 88 and 98 %. Other aliphatic amines and NH_3 can be collected and quantified on the same tube. Unequivocal confirmation of MEA in complex matrices can be made with MS.	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).	GC-FID Column: glass 2 m x 2 mm packed with Chromatone N (0.16 – 0.20 mm) coated with polysiloxane OV-225 (5 %).	Estimated 0.2 mg/m^3	Interferences: NH_3 and other amines that react with H_2SO_4 and decrease the chemisorption capacity of the tube. In particular, DEA and TEA.	Low maturity: Article (Zenkevich & Chupalov 1996)
working atmosphere; aqueous solutions, urine	Piperazine specific	Q	Two-phase derivatization with ethyl- or isobutyl chloroformate in presence of NH_3. NH_3 insured a quantitative recovery. Evaporation prior to chromatography (especially important for method (1) to avoid influences on the sensitivity of the detector). LLE procedures might be used instead of evaporation.	(1) GC-nitrogen selective detector (2) GC-MS Several columns were used: Duran 50 borosilicate glass capillary column (15 m x 0.32 i.d.) coated with PS-255 (film thickness 0.75 µm) (1). Two other columns for (1) and (2): Chromopack Aryl 17 CB (15 m x 0.32 i.d., film thickness 0.15 µm) and Chromopack CP-Sil 8CB (25 m x 0.32 i.d., film thickness 1.1 µm) both chemically bonded.	Aqueous solutions < 3 pg/µl	Linearity range (ng/ml): (1) 100-10000 (2) 30-3000 Alternative derivatization agent for aqueous solution: heptafluorobutyric acid anhydride. In this case no evaporation / extraction step I required.	Low maturity: Article (Skarping et al.1986)

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
air	AMP specific	Q	Sampling on glass tubes containing XAD-2 resin coated with 10 % (w/w) 1-naphthylisothiocyanate (NIT). NIT works as derivatization agent forming a stable derivative. Extraction with dimethylformamide.	LC-UV. Column: 4.6 x 250 mm column packed with 5 µm Bakerbond cyanopropyl (JT Baker). Mobile phase: 80:20 isooctane : isopropanol.	Overall 0.04 ppm based on 10 l air volume.	Desorption efficiency from sampling tubes mean of 100 % in the range 224 to 11.2 µg/tube. The mobile phase used gave a good separation of the AMP peak form interferences from NIT. 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. Suggested confirmation method: LC/MS.	Medium maturity: OSHA method PV2145. Partially Validated.
air	DEA 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.	HPLC-UV. Column: 10u Radial CN, 10 cm x 8 mm i.d. Mobile Phase: 80:20 isooctane:isopropanol.	Overall 0.04 ppm based on 10 l air volume.	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.
air	MEA 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.	HPLC-UV. Column: 10 µm Zorbax CN, 25 cm x 4.6 mm i.d. Mobile Phase: 80:20 isooctane:isopropanol.	Overall 0.06 ppm based on 10 l air volume.	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.

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	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.	HPLC-UV. Column: 10 µm Radial CN column (100 mm x 8 mm i.d.). Mobile Phase: 80:20 isooctane:isopropanol for EDA. (50:50 for TETA and DETA).	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.
air	MEA, DEA. Primary and secondary alkanolamines in air.		Sampling on silica gel tubes, desorption with 4:1 MeOH:water under acidic conditions. Derivatization with 9-fluorenyl methyl chloroformate (FMOC) in basic alcohol aqueous media (1:1 acetone:acetonitrile). Extraction with pentane to remove excess FMOC.	Reverse phase HPLC-FL Column: 25 cm x 4.6 mm i.d. 5 µm Supercosil LC-8 column. Mobile phase: containing acetonitrile, acetic acid and water.	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 increasing with the amount of alkanolamine in the sample. Good storage stability of the samples.	Low maturity: Article (Serbin & Birkholz 1995)
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.	HPLC/ESI-MS Electrospray Ionization (ESI). Column: Phenomenex Luna C_{18} (3 µm, 150 x 2.0 mm). Mobile phase: Acetonitrile + 1% formic acid and water.	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 $1.5\cdot10^7$, MEA $1.7\cdot10^7$, MMA $3.4\cdot10^7$, DMA $4.2\cdot10^7$ 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)

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
air	MEA, DEA, (triethanolamine). Aminoethanol compounds.	Q	Sampling: IMPINGER. Elution with hexanesulfonic acid.	IC Column: ion pairing guard and cation separator Dionex MPIC-NG1, MPIC-NS1, cation suppressor. Eluent: 2 mM hexanesulfonic acid.	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 ammonium ions may interfere with MEA.Method evaluated for DEA. Recovery: 70-95 %.	Medium maturity: NIOSH method 3509. Partially evaluated. (NIOSH 1994e)
Matrix not specified	MEA, DEA (triethanolamine).	Q	Chemiluminescence catalyzed by copper (II) or cobalt (II) (pre- column).	LC-CL (chemiluminescence, based on detection with luminol reaction, post -column) Column: 25 cm S5 ODS-2 reversed-phase column (Spherisorb). Mobile phase: hexane, sulfonic acid, water.	MEA 0.8, DEA 1.2 nmol		Low maturity: Article (Worsfold & Yan 1991)
aluminum chemical etching process samples. Suitable for complex matrices and environmental samples.	Alkanolamines (Tested on triethanolamine)	Q	Dilution.	LC-PAD (Pulsed Amperometric Detector) Column: reversed phase Dionex Omni-Pac PAX-500 with the anion-exchange resin in the hydroxide form. Eluent: NaOH + ACN. PAD: Gold working electrode, stainless steel counter electrode and silver/silver chloride reference electrode.	TEA and other alkanolamines 1 ppb	ACN in high pH is decomposed to acetic acid and other nitrogen containing compounds that might interfere with the detector response. Since the reaction of ACN in NaOH is slow, it is sufficient to change the eluent every 8 h to optimise the instrument performances. Linearity (TEA): 1-100 ppm with r^2 = 0.9992.	Medium maturity: Article. This method was used as standard at Boeing Company Airplane Group (USA) for the determination of TEA. (Campbell et al. 1991)

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
filtered water extracts of vegetation	MEA, DEA, MDEA (DIPA).	Q	Ionization of the amine by means of acetic acid.	ESI/LC/MS and ESI/LC/MS/MS (confirmation of amines and degradation products). Column: 25 cm x 2 mm i.d. IonPac CS14 cation exchange column. Eluent: 50:50 MeOH:water with 1 % formic acid.	Generally < 0.02 ppm. Instrumental DL in the range of 20-40 pg.	Linear calibration curves (for DIPA) in the range 0-1 µg/l. Recovery of DIPA 89.7 %. Interferences: glycols and glycolamines (monoethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol). These interferences can be eliminated by higher mass resolution. In the case of DEA, diethylene glycolamine can interfere; an improved chromatographic separation is needed in this case.	Low maturity: Article (Headley et al. 1999)
water, human urine, serum	EDA, MMA, EA. Aliphatic primary amines and diamines.	Q	Water was filtered prior to derivatization. Pre-column derivatization with 2, 6-dimethyl-4-quinolinecarboxylic acid N-hydroxysuccimide ester (DMQC-OSu).	HPLC-FL Reverse phase chromatography. Column: 150 x 4.6 mm i.d. 5 µm particle Eclipse XDB-C_{18} column. Eluent: contained water and MeOH	MMA 0.02, EA 0.02, EDA 0.02 nmol/l Reliable real water sample quantification in the range 0.07-4 nmol/l.	Linearity range: 1-80 (nmol/l). R^2 = 0.9999 for MMA and EA, 0.9994 for EDA. Interferences: DMQC-OSu reacts with amino acids but do not interfere with the chromatography analysis. No interferences from alcohols were found.	Low maturity: Article (Huang et al. 2009)
surface water and waste water	Piperazine. Aliphatic and alicyclic amines-> C_3 may be possible also for < C_3	Q	2 different methods are included. Only the HPLC-method suits piperazine. Sample preparation schemes (enrichment and derivatization) are described in the article. Derivatization in HPLC-method with 9-fluorenylmethyl chloroformate.	HPLC- fluorescence detector, Column Macherey-Nagel ET- (150 mm/ 4 mm/ 8 mm Nucleosil packed with 5 µm C18 material). Eluent: acetonitrile in water.	HPLC: 0.03 µg/l for piperazine	RSD: 1.7 % R^2= 0.9999 for piperazine.	Low maturity: Article (Pietsch et al. 1996)

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
lake water	MMA, EA, MEA, DMA. Primary and secondary aliphatic amines and alkanolamines.	Q	Derivatization with N-hydroxysuccinimidyl 4,3,2´-naphthapyrone-4-acetate.	Reversed-phase- HPLC with spectrofluorimetric detection. Column: Lichrosorb RP-C_8 250 x 4.6 mm i.d. 10 µm, Merck.	MMA 2.4, EA 5.1, MEA 2.1, DMA 16 fmol/20 µl injection	The presence of salt and other organic substances in the water samples does not interfere with the analytical method. Linearity range (µmol/l): 0.01 – 1.0. Linearity r^2: MMA 0.9999, EA 0.9995, MEA 0.9990, DMA 0.9972.	Low maturity: Article (Liu et al. 2001)
plant tissue	MMA, EA, DMA, alkanolamine MEA, ammonia and other amines	S	Suitable pre-treatment not specified for desired matrices. Derivatization with dansyl chloride with amines in aqueous solution.	HPLC-UV/VIS Column: Brownlee Spheri-5 RP-18 C_{18} (5µm, 250x4.6mm).	Varied with the relative intensities, generally of 5 – 10 pmol.	Linear in range of 2 -16 µM for all the other amine except ammonia, MMA and DMA.	Low maturity: Article (Price et al. 1992)
water	DMA, DEN, and secondary aliphatic amines also alkanolamine DEA	Q	Pre-treatment, depending on the amine matrix, explained. Derivatization with 5-isothiocyanato-1,3-dioxo-2-p-tolyl-2,3-dihydro-1H-benz[de]isoquinoline (MCPBA), followed by oxidation with 3-chlorobenzoic acid to form corresponding formamidines.	HPLC-fluorescence detector Column Lichrospher RP-18 (300 x 4 mm, 5 µm particles).	200-300 fmol (20 µl injected)	The samples were stable in brown glass vials. The stability of the derivatives (formamidines) was about 1 h. The detector signal was linear for all formamidines tested over the range from 0.5 to 20pmol (>0.997).	Low maturity: Article (Khalaf & Steinert 1996)

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
blood, shaving gel	Alkanolamines	Q	Dilution (for blood and shaving gel).	HPLC-PED (Pulsed Electrochemical Detector) Column: cation-exchange reverse-phase retention mode, either a full-size (250 x 4 mm) or guard size (50 x 4 mm) PCX-500. Pulsed voltametry was performed at the gold disk. The counter electrode was a coiled platinum wire. Mobile phase: containing NaOAc and eventually CAN.	For 25 µl injection: 20 nM (TRIS).	Method tested with tris(hydroxylmethyl)aminomethane. Linear in the range 50 nM to 100 µM (r^2 = 0.9997).	Low maturity: Article (Dobberpuhl & Johnson 1995)
residual water, river water and human urine	MMA, EA, DMA, DEN, TMA, TEA and alkanolamines EDA, MEA. Ammonia and other aliphatic amines	M	Samples are filtered and reagent solution m-nitrobenzene is added.	Spectrofotometer	MMA 0.5, EA 1.0 DMA 1.0, DEN 0.5, TMA 0.5, TEA 2.0 EDA 1.0, MEA 1.0 mg/l	Maximum concentration detected (mg/l): MMA 10, EA 6 DMA 6, DEN 8, TMA 10, TEA 8, EDA 6, MEA 5	Low maturity: Article (Siddiqi & Pathania 2003)
aquarium and river water	MMA, EA, DEN, alkanolamine MEA, ammonia and other aliphatic amines.	Q	Centrifugation on filtration to remove solids. Derivatization with 4-chloro-7-nitrobenzo-2-oxa-1,3-diazole (NBD-Cl)	MEKC-LIF (micellar elektrokinetic chromatography with laser induced fluorescence detection) Column: fused-silica 57 cm (50 cm to the detector) x 75mm	MMA 0.2 MEA 0.1 EA 0.1 DEN 0.1 ng/ml	The signal response was linear over three-order of concentrations (r^2 > 0.99) Range (µg/l): MMA 0.03-6, MEA 0.01-6.0 EA 0.015-6, DEN 0.01-12 Recovery: 90.2 – 110.8 % RSD for peak area: 1.76-2.01 % LQ (ng/ml): MMA 0.7, MEA 0.3 EA 0.3, DEN 0.3	Low maturity: Article (Hui et al. 2010)

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
pharmaceuticals substances	Method optimized for hydroxylamine. MMA, EA, MEA, DEA. Small amines: alkylamines and alkanolamines + other amines and ammonium.	Q		CIE with direct conductivity detection. ConCap^{TM} I fused silica capillaries, 50 µm i.d. x 375 µm o.d. x 60 cm. Buffer: 30 mM MES – 30 mM glycylglycine.	1 ppm only given for hydroxylamine.	Linearity range: 0.05 – 0.5 mM, $r^2 > 0.99$	Low maturity: Article (Bowman et al. 2000)
refinery process waters	MDEA or DEA in presence of high ammonium content.	Q		CE-UV Capillary electrophoresis with indirect UV detector. Background electrolyte (BGE): 10 mM histidine adjusted to pH 5.0 with acetic acid. Bare fused-silica capillaries, 75 µm i.d., effective length 28.9 cm and total length 37.3 cm.	MEA 0.2, DEA 0.7 ppm	Suitable up to 300 ppm of DEA and MDEA in presence of high levels of NH_3 (2000-6000 ppm) and hydrogen sulfide (2000-10000). Linearity was tested with ANOVA 95% test. Recovery %: DEA 105, MDEA 100.	Low maturity: Article (Bord et al. 2004)
aqueous solutions, metal working fluids	AMP, DEA, MEA, PIP. Formaldehyde releasers.	Q		CE-MS Capillary: uncoated fused-silica capillary tube 75 µm i.d., 57 cm total length and 50 cm effective length. Ammonium acetate/ acetic acid buffer.	AMP 0.2, DEA 0.1, MEA 1.2, PIP 0.2 mg/l.	Linearity range 5-50 mg/l with $r^2 > 0.99$. MDEA was undetectable with this CE-MS method. MDEA was detected with CE-DAD but it was not baseline-separated from DEA and AMP. The higher LD for MEA is caused by the m/e interference of the separation electrolyte.	Low maturity: Article (Fekete et al. 2006)

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
alkanolamine solutions from sweetening plants	MEA, AMP, MDEA, DEA and other alkanolamines. Analysis of fresh and degraded alkanolamine solutions from gas sweetening plants.	Q		GC Finding the best column. Column (best): Supelcowax 10, a polyethylene glycol-based, fused-silica, cross-linked, bonded-phase capillary column (15 m x 0.53 mm i.d., 1.0 µm film thickness).		The results showed that polar polyethylene glycol – based, wide-bore, fused silica, bonded-phase capillary columns are suitable for analyzing fresh and partially degraded alkanolamine solutions. In particular, their superiority on Tenax packed columns is demonstrated.	Low maturity: Article (Dawodu & Meisen 1993)
lean water + MEA solution and reclaimed bottoms of amine sweetening units	MEA and its degradation products. Total nitrosamine concentration also analyzed.	Q		(1) GC-MS (2) GC-FTIR (Fourier transform infrared adsorption spectrophotometry) (3) GC-AED (atomic emission detection) Columns: 60 m x 0.32 mm i.d. fused silica column coated with 0.25 µm film of 14 % cyanopropyl-phenylmethylpolysiloxane. (DB-1701). 60 m x 0.25 mm i.d. column coated with 0.25 µm film of nitro-terephthalic acid- modified poly(ethylene glycol), (Nukol).		This article gives a good overview of the analysis of rich/lean amine solvent by means of the combined use of several analytical techniques. The total amount of nitrosamines was also analyzed with the method described in (Ding et al. 1998). The inorganic ionic species were analyzed by IC.	Low maturity: Article (Strazisar et al. 2003, Ding et al.1998)

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
CO_2 loaded water + MEA solutions also in presence of O_2	MEA and its degradation products. Among the degradation products are found: acetamide, formamide, ethylamine, acetaldehyde etc.	Q	(1) GC-MS Sample dilution (1 in 5) (2) HPLC-RID Sample dilution (1 in 40) Filtration. (3) CE-DAD Sample dilution (1 in 500) Filtration.	Three methods tested: (1) GC-MS Columns: HP-35MS (intermediate polarity) best in analyzing the degradation products. HP-Innowax (high polarity) was best for analyzing MEA. Dimensions of the columns: 0.25 µm thickness x 0.25 mm i.d. x 30 m length. (2) HPLC-RID (Refractive Index Detector) Column: Nucleosil 100-5 SA 250 mm x 4.6 mm i.d. Mobile phase: potassium dihydrogen phosphate solution adjusted to pH 2.6 by phosphoric acid. (3) CE-DAD (Diode array detector) using phosphate and borate electrodes detected the degradation products.		This article gives a good overview on the problem concerning the analysis of rich/lean amine solvent. (2) was the best and only technique in which simultaneous analysis for MEA and its degradation products. It detected 7 degradation products. (1) was able to detect either the degradation products (16 products) or MEA depending on the column. (3) only detected the degradation products (8 products).	Low/medium maturity: Article (Supap et al. 2006) Method (1) also in references: (Supap et al. 2001, Bello & Idem 2005)
degraded aqueous solutions of DEA from gas sweetening units	DEA and its degradation products. MEA (TEA)	Q	No sample preparation needed.	GC-FID Column: 6 ft. x 1/8 in. o.d. stainless-steel column packed with 60-80 mesh Tenax GC.	0.5 wt%	11 degradation products were detected. Accuracy typically 5 %.	Low maturity: Article (Kennard & Meisen 1983)

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
amine sweetening process liquids and wastewater from such plants	MEA, DEA, MDEA. Wash amines and their degradation products, including ammonium ions.	Q	Water dilution since the concentration of the determined compounds should not be above 1.5 wt%. Filtering.	Cation-exchange HPLC-RID. Column: 250 x 4.6 mm Macherey – Nagel HPLC packed with Nucleosil SA 5 µm. Mobile phase: 0.088 M aqueous solution of KH_2PO_4 acidified with 85 % H_3PO_4 to pH 2.6.	For 20 µl sample: Ammonium ion 0.012, MEA 0.0025, DEA 0.0033, MDEA 0.004 %.	Total determination time: 10 min. Linearity: 0.01-1.5 wt% with $r^2>0.998$. The addition of acetonitrile to the eluent reduced the retention of alkanolamines. UV or UV-DAD can be used in series with RI to determine simultaneously other substances, like aromatic amines.	Low maturity: Article (Kaminski et al. 2002)
gas sweetening absorption solution; water and wastewater	MEA, DEA, MDEA, Piperazine and other alkanolamines.	Q		IC-PED (Ion Chromatography with Pulsed Electrochemical Detector). Columns (always a guard and an analytical column): IonPac CS10 and CS12A (250 x 4 mm) separator columns and IonPac CG10 and CG12A (50 x 4 mm) guard columns. Eluent: sulfuric acid		IC can also be used to determine short chain aliphatic amines in presence of alkanolamine in wastewater with low salinity. The best column for aqueous matrices was found to be the CS10. The separation of piperazine in aqueous solution in presence of MDEA (rich/lean amine solvent) was the best with the CS12A column. The method is also useful to determine piperazine in water samples or MDEA in scrubber solutions. Interferences: salt, alkaline hearth metals.	Low maturity: Article (Kadnar 1999)

4.4 Analysis of amides

The amides of interest in this study are LMW amides, acetamide and formamide. There is little information in the literature on the analysis of acetamide and formamide in the matrices of interest. Due to the low molecular weight of these amides, LC methods may not be feasible (Diekmann et al. 2008). There was in fact no mention of such analytical methods found in the literature. Gas chromatography appears as the best option. OSHA published a partially validates stopgap method for the determination of acetamide in air (OSHA method 2084) that uses GC equipped with a nitrogen phosphorous detector. A GC-UV method was also found for acetamide in air. Formamide has a strong UV absorption at wavelengths close to 200 nm (Porras & Kenndler 2004), therefore GC-UV might be suitable also for formamide analysis. GC-MS is the most commonly found analytical method for these amides, when they are analyzed with other VOCs (volatile organic compounds) in air or in liquid matrices, often biological such as blood. Neither ISO nor ASTM standard methods were found for the components of interest.

Table 7 Analytical methods for amides (Method type: Q=quantitative, MeOH=methanol).

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
(air)	Acetamide specific	Q	Sampling with silica gel tube. Desorption with MeOH.	GC-NPD (nitrogen phosphorous detector) Column: 6 ft 10 % UCON 50-HB-5100 on 80/100 Chrom WAW with 2% KOH.	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. Partially Validated. Stopgap method.
dust particles	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).	GC-UV Miniaturized GC column: 80 x 1.5 mm column packed with 10 µm Nucleosil NH and OV17 (Alltech, USA). Nitrogen-flushed photo diode array (PAD) detector for fast UV spectra recording. GS-MS was also used.			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.	GC-MS GC with on-column injection. Column: 30 m J&W Scientific free fatty acid phase fused silica capillary column with 0.25 mm i.d. and 0.25 µm film thickness.	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.	GC-MS Column: 50 m x 0.22 mm, 1 µm. The stationary phase is a modified siloxane polymer with 5% phenylsiloxane.			Low maturity: Article (Karpe et al. 1995)
air	Acetamide. VOC	Q	Sampling and pre-treatment for swine barn particulate. Analysis of VOC extracts.	GC-MS Column: non-polar pre-column and polar column in series.			Low maturity: Article (Cai et al. 2006)

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
wastewater sludges)	Acetamide in a complex matrix.	Q	Pre-treatment for wastewater sludges (pyrolisis).	GC-MS Column: fused silica capillary column (0.32 mm i.d. film thickness 0.5 µm) with a polar capillary phase (column SolGelWax, SGE).			Low maturity: Article (Parnaudeau & Dignac 2007) GC-MS was used also in the work by (Li & Zou 2006) and (Ramirez et al. 1998)
whole blood	Acetamide	Q	Pre-treatment for blood. Extraction with acetonitrile-ethanol.	GC-MS Column: DB Wax (60 m x 0.32 mm i.d.) with a stationary phase thickness of 0.5 µm.	5 µg/ml.	Recovery of acetamide from blood by extraction gave recovery of about 70 %.	Low maturity: Article (Lindstroem et al. 1988)

4.5 Analysis of aldehydes

Trace analysis of LMW reactive carbonyl compounds (RCCs) such as formaldehyde and acetaldehyde is a difficult experimental procedure due to their high reactivity and high solubility in water (Shibamoto 2006). For this reason, there is a great amount of literature available on the subject. The analytical methods presented in this report are a collection of methods that represent the various directions taken by researchers in recent years. Validated methods of analysis by associations such as NIOSH, OSHA and EPA are also presented. The collected analytical methods were developed for the analysis of acetaldehyde and formaldehyde in air and aqueous matrices, and are considered suitable for flue gas and 2. No analytical aldehydes detection methods specifically developed for a matrix similar to 3 were found in the literature.

LMW aldehydes are very difficult to be extracted from an aqueous solution with organic solvents because they are soluble in both water and lipids. Therefore, these aldehydes are often derivatized into more stable and less reactive compounds. In the case of air samples, derivatization usually takes place during sampling. In the case of water samples, after derivatization a sample concentration step is often required. The most commonly used derivatization agent for formaldehyde and acetaldehyde is 2,4-dinitrophenylhydrazine (DNPH) to form hydrazones (Shibamoto 2006). The derivatives are analyzed by chromatographic techniques as well as by spectrophotometry (NIOSH 1994g). GC is coupled with a variety of detectors such as FID, NPD and MS. Since some of the RCC-DNPH derivatives are not very volatile, research has changed in the direction of improving LC and HPLC methods (Shibamoto 2006). LC and HPLC are usually coupled with MS or UV detectors. Disinfected water was analyzed for aldehydes, also without sample preconcentration, by means of HPLC-electrospray ionisation (ESI)-MS /MS (Zwiener et al. 2002). An EPA method using DNPH derivatization and HPLC is available for water samples (EPA 1996c).

Air samples of aldehydes are collected with liquid impingers, sampling cartridges or filters (Bingham et al. 2001). NIOSH and OSHA analytical methods for formaldehyde and acetaldehyde analysis in air mostly use sampling by chemical absorption on a solid sorbent coated with the derivatization agent, followed by extraction and analysis. 2-(hydroxymethyl) piperidine (2-HMP) have been used as derivatization agent when GC is used, coupled with FID, NPD and MS. DNPH is used instead with LC-UV, HPLC-UV, VIS and MS. HPLC-ESI-MS/MS was also used to analyze air samples (Chi et al. 2007).

Standardized methods for the determination of aldehydes in air samples use DNPH derivatization and HPLC analysis (Hafkenscheid & van Oosten 2002). A standard method for the determination of formaldehyde and other carbonyl compounds in air is published by the U.S. EPA (EPA 1999) and it uses air collection on DNPH coated cartridges, followed by solvent desorption with acetonitrile and analysis with HPLC-UV. DNPH coated samplers suffer from potential interferences from co-pollutants such as ozone that consumes DNPH and degrades the derivatives (Bingham et al. 2001, NIOSH 1994h). Ozone is often removed by an ozone trap during sampling. A study (Grosjean & Grosjean 1996) was published on the carbonyl collection efficiency of DNPH-coated C_{18} cartridges in air. The results showed good performances of these cartridges in humid air, but poor sampling performances in very dried air especially for formaldehyde.

Alternative derivatization agents are continuously developed by researchers in order to find a substance able to improve the analytical performances obtainable with DNPH. An interesting derivatization agent for low molecular weight aldehydes is pentafluorophenyl hydrazine (PFPH) that gives more volatile derivatives than DNPH. A comparison study of PFPH/GC and DNPH/HPLC-UV methods applied to formaldehyde and acetaldehyde showed that PFPH/GC could reach lower detection limits (Shibamoto 2006 et al. 2004). A more recent derivatization agent for LMW aldehydes is cysteamine that gives thiazolidine derivatives that can be analysed by GC, e.g. GC/FPD (Kataoka et al. 1995, Kataoka et al. 1997).

ISO 16000-3:2001, ISO 16000-4:2004 and ISO 16000-6:2004 are standard ISO methods for the determination of formaldehyde in indoor air. ISO 16000-3:2001 is an active sampling method,

ISO 16000-4:2004 specifies a diffusive sampler/solvent desorption/HPLC procedure and ISO 16000-6:2004 uses active sampling on Tenax TA sorbent, thermal desorption and GC using MS/FID. Formaldehyde is analyzed in solutions for industrial use by means of ISO 2227:1972. ASTM D5197 - 09 is a standard test method for the determination of formaldehyde, acetaldehyde and other carbonyl compounds in air using active sampling.

4.5.1 Pre-treatment

In the case of water samples many methods, including the EPA method for aqueous matrices (EPA 1996c), concentrate the sample by means of solid phase extraction SPE. Among the materials used are poly(dimethylsiloxane)-coated fibers (Bao et al. 1998), divinylbenzene-polydimethylsiloxane (Cancho et al. 2002, Stashenko et al. 2000) and Oasis HLB cartridges (Zwiener et al. 2002). Poly(allylamine) beads were also studied for this purpose (Kiba et al. 2000). A comparative study of six conventional and non-conventional sorbent materials was carried out for the concentration and simultaneous derivatization of aldehydes with DNPH. LiChrolut EN and RP-C_{18} were found to be the most suitable sorbents for the concentration of aldehydes. LiChrolut EN, in particular, showed the highest efficiency for the in situ derivatization and superior performance in terms of sensitivity (Banos & Silva 2009a).

Table 8 Analytical methods for aldehydes (Method type: Q=quantitative, S=Screening, MeOH=methanol).

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
air, bulk field samples	Acetaldehyde, formaldehyde. Aldehydes.	S	Sampling and derivatization on sorbent tubes (10 % 2-(hydroxymethyl) piperidine (2-HMP) on XAD-2, 120 mg/ 60 mg). 2-HMP is the derivatization agent. Desorption with toluene.	GC-FID and (GC-MS for confirmation). Column: capillary, 15 m x 0.32 mm, 1.0 µm film 6% cyanopropyl- phenyl, DB-1301 or equivalent. Analyte: oxazolidine derivatives of aldehydes.	Estimated 2 µg aldehyde per sample.	Alternate column such as DB-WAX can be used for GC-MS confirmation.	Medium maturity: NIOSH method 2539. Partially validated. (NIOSH 1994c)
air	Acetaldehyde specific	Q	Sampling and derivatization on sorbent tubes (2-(hydroxymethyl) piperidine (2-HMP) on XAD-2, 450 mg / 225 mg). 2-HMP is the derivatization agent. Desorption with toluene.	GC-FID Column: wide-bore, fused-silica capillary, 15 m x 0.32 mm, 1.0 µm film DB-1301. Alternative column: 2 m x 6 mm o.d. x 2 mm i.d. glass column containing 10 % UCON 50-HB-5100 + 2 % KOH on 80/100 Chromosorb W-AW. Analyte: oxazolidine derivative from acetaldehyde.	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 of refrigerated storage. A method using GC-FID without derivatization step for carbonyl compounds in air (tested on acetaldehyde) in described in (Pal & Kim 2008, Kim & Pal 2010).	High maturity: NIOSH method 2538. Evaluation: unrated. Modification of OSHA method 68 (NIOSH 1994a, OSHA method 68)
air	Acetaldehyde specific	Q	Sampling and derivatization on sorbent tubes (2-(hydroxymethyl) piperidine (2-HMP) on XAD-2, 450 mg sampling section/ 225 mg backup section). 2-HMP is the derivatization agent. Desorption with toluene.	GC-NPD Column: 6-ft. x ¼ in. o.d. (2 mm i.d.) glass column containing 10 % UCON 50-HB-5100 with 2% KOH on 80/100 mesh Chromosorb W-AW. On-column injections. GC-MS is the suggested method of confirmation.	Reliable LOQ (and LOD): 1050 µg/m^3.	Derivatization of acetaldehyde with 2-HMP gave two derivatives, both having the same molecular formula. 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. Fully validated.

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
air	Formaldehyde (and Acrolein)	Q	Sampling and derivatization on sorbent tubes (2-(hydroxymethyl) piperidine (2-HMP) on XAD-2). 2-HMP is the derivatization agent. Desorption with toluene.	GC-NPD Column: 6 ft. x ¼ in. o.d. (2 mm i.d.) glass GC column containing 10 % UCON 50-HB-5100 with 2 % KOH on 80/100 Chromosorb W-AW. GC/MS is the recommended method of confirmation.	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. Fully validated.
air	Formaldehyde (and acrolein)	Q	Sampling and derivatization on sorbent tubes (2-(hydroxymethyl) piperidine (2-HMP) on XAD-2, 120 mg / 60 mg). 2-HMP is the derivatization agent. Desorption with toluene.	GC-FID Column: capillary 30 m x 0.32 mm i.d., 0.5 µm film, DB-Wax. Analyte: oxazolidine derivative of formaldehyde. Alternative column: 15 m x 0.32 mm i.d. DB-1301 fused silica capillary column. NPD detector can be used for improved sensitivity.	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.	Medium maturity: NIOSH method 2541. Partially Validated. (NIOSH 1994f)
air	Formaldehyde, acetaldehyde and other carbonyl compounds	Q	Sampling and derivatization onto 2,3,4,5,6-pentafluorophenyl hydrazine (PFPH) coated solid sorbents. PFPH is the derivatization agent. Thermal desorption (TD).	GC-MS Column: HP-5MS column (5% diphenyl/ 95% diethyl polysiloxane, 30 m x 0.25 mm i.d. x 0.25 µm film thickness).	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/medium maturity: Article (Ho & Yu 2004) A similar method is also proposed by (Li et al. 2009)
cigarette smoke and food samples	Aliphatic and aromatic aldehydes	Q	Derivatization with cysteamine into thiazolidine derivatives.	GC-FPD Column: two connected fused silica capillary columns. DB-17 (15 m x 0.53 mm i.d., 1.0 µm film thickness) and DB-210 (15 m x 0.53 mm i.d., 1.0 µm film thickness).	4-100 pg injected	Linearity range: 20 – 2500 ng.	Low maturity: Article (Kataoka et al. 1995, Kataoka et al. 1997)

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
air	Formaldehyde, acetaldehyde (and other aldehydes and ketones)	Q	Sampling with an air sampler pump. Derivatization with 4-dimethylamino-6-(4-methoxy-1-naphtyl)-1,3,5-triazine-2-hydrazine (DMNTH). The sampler's impingers contained the DMNTH solution.	HPLC-MS Column: Discovery C_{18} column equipped with a guard column of the same material (Supelco). Dimensions: 5 µm particle size 100 Å pore size, 150 mm x 2.1 mm i.d. Mobile phase: Eluent A: triethylamine, acetic acid and water. Eluent B: acetonitrile. All MS measurements were recorded using APCI (Atmospheric Pressure Chemical Ionization) positive mode.	formaldehyde $5 \cdot 10^{-8}$ mol/l, acetaldehyde $2 \cdot 10^{-8}$	Linearity was observed up to $5 \cdot 10^{-5}$ 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.	HPLC-MS Column: C18 150 mm x 3 mm and 5 µm particle size, with a 2 cm x 3 mm pre-column of the same packing. MS measurements were recorded using APPI (Atmospheric Pressure Photoionization) mode. Comparison with APCI mode is given.	*APPI mode:* LOD: formaldehyde $24 \cdot 10^{-9}$ M, acetaldehyde $8.8 \cdot 10^{-9}$ M LOQ: formaldehyde $80 \cdot 10^{-9}$ M, acetaldehyde $29 \cdot 10^{-9}$ M, *APCI mode:* LOD: formaldehyde $70 \cdot 10^{-9}$ M, acetaldehyde $73 \cdot 10^{-9}$ M, LOQ: formaldehyde $234 \cdot 10^{-9}$ M, acetaldehyde $244 \cdot 10^{-9}$ 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	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	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.	HPLC-UV (DAD) Column: Reverse phase Nova-Pak C_{18}, 4 µm particles, 150 mm x 3.9 mm i.d.	For typical sample (750 l): 0.01 – 0.05 $\mu g/m^3$	Range of use: 0.1 – 10 $\mu g/m^3$.	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. Dilution with HPLC mobile phase.	HPLC-UV Column: 50 cm x 2 mm I.D SS, Zipax SCX Mobile phase: Na_2HPO_4 / NaH_2PO_4 buffer.	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.	High maturity: NIOSH method 3507. (NIOSH 1994b) Fully Validated

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
air	Formaldehyde specific	Q	Sampling and derivatization on cartridges containing silica gel and coated with 2,4-dinitrophenylhydrazine (2,4-DNPH, derivatization agent). Elution with carbonyl-free acetonitrile. Acetonitrile should be checked for formaldehyde content by elution and analysis of a ablank cartridge and it should be below the detection limits.	HPLC-UV Column: 3.9 x 150 mm, stainless steel, packed with 5 µm C-18 Symmetry. Mobile phase: 45 % acetonitrile / 55 % water (v/v). Analyte: 2,4-dinitrophenylhydrazone of formaldehyde.	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.	High maturity: NIOSH method 2016. (NIOSH 1994h) 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). 2,4-dinitrophenil hydrazine (DNPH) in presence of a strong acid is the derivatization agent. Formaldehyde gives a unique derivative. Elution with acetonitrile.	LC-UV Column: Pinnacle TO-11 5µm 250 x 4.6 mm (Restek corporation). Mobile phase: 35% water / 65% acetonitrile / 0.2% phosphoric acid (v/v/v). Suggested method of confirmation: GC/MS.	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. Fully Validated.

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
air	Formaldehyde(acetal dehyde and other carbonyl compounds)	Q	Sampling and derivatization with a pre-packed cartridge coated with acidified DNPH. Elution with acetonitrile.	HPLC-UV Column: Zorbax ODS reverse phase (RP) column (25 cm x 4.6 mm i.d.). Two column in series are used when also other carbonyl compounds than formaldehyde are identified.	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.	HPLC-UV/Vis Column: 250 mm x 4.6 mm i.d. 5 µm particle size, C_{18} column, Zorbax or equivalent. Mobile phases: containing acetonitrile and water. For ambient air samples: two columns in series and different mobile phases are used.		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 1996c, 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.	HPLC-ESI-MS/MS Column: Agilent Zorbax Eclipse XDB-C18 column (250 mm x 4.6 mm, 5 µm). Mobile phase: a mixture of acetonitrile, water and ammonium acetate.	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	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	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.	CE-UV and CE-LIF (Laser Induced Fluorescence Detector) Capillary: fused silica, 58 cm (50 cm effective length) x 75 µm i.d. x 375 µm o.d.	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.	CE-DAD Capillary: fused silica, 58 cm (50 cm effective length) x 75 µm i.d. x 375 µm o.d Background electrolyte: pH 9.3 tetraborate buffer.	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	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
air	Formaldehyde specific	Q	Sampling with filter + impingers (1 µm PTFE membrane and 2 impingers, each with 20 ml 1 % sodium bisulfite solution).	VIS (Visible Absorption Spectrometry)	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.	High maturity: NIOSH method 3500. (NIOSH 1994g) Fully Validated
water	Acetaldehyde, formaldehyde (and other carbonyl compounds)	Q	Derivatization with o-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine hydrochloride (PFBHA) and extraction with SPME (100 µm poly(dimethylsiloxane)-coated fiber mounted in a manual syringe holder, Supelco). Two SPME techniques tested: liquid SPME and head space SPME. The sensitivity of the two techniques was similar for acetaldehyde and formaldehyde.	GC-ECD (Electron Capture Detector) Column: 30 m x 0.25 mm i.d. 0.25 µm film thickness, SPB-5 fused-silica capillary column (Supelco).	Liquid SPME: acetaldehyde 0.02 µg/l and formaldehyde 0.015 µg/l. Headspace SPME: acetaldehyde 0.03 µg/l and formaldehyde 0.02 µg/l	Linearity range: 0.1 – 100 µg/l with $r^2>0.989$. Headspace SPME gives cleaner extracts than liquid SPME. LLE can be used as extractive method.	Low maturity: Article (Bao et al. 1998)

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
water	Acetaldehyde, formaldehyde (and other aldehydes)	Q	Derivatization with *o*-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (PFBOA).	HS-GC-MS (Head Space) Column: PTE-5TM of Supelco, fused silica capillary column 30 m x 0.25 mm x 0.25 µm film thickness.	acetaldehyde 0.5 µg/l and formaldehyde 0.5 µg/l	Salting-out effects studied: addition of 3 g NaCl to 10 µg/l of aldehyde standard solution increased the sensitivity 2 to 3 times.	Low maturity: Article (Sugaya et al. 2001)
water	Acetaldehyde, (and other carbonyl compounds)	Q	Derivatization with *o*-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine hydrochloride (PFBHA) and HS-SPME with divinylbenzene-polydimethylsiloxane coating (DVB-PDMS).	GC-ECD (Electron Capture Detector) Column: DB-1701 fused-silica column with 1.0 µm film thickness, 30 m x 320 µm i.d.	acetaldehyde 0.04 µg/l	Salting-out effects studied: addition of 6 g NaCl gave the best extraction of carbonyl compounds. Linearity range: 0.5 – 19.4 µg/l r^2=0.996 for acetaldehyde.	Low maturity: Article (Cancho et al. 2002)
water	Acetaldehyde, formaldehyde (and other carbonyl compounds)	Q	Derivatization with DNPH. SPE pre-concentration: two procedures given: (1) SPE in situ derivatization/ pre-concentration (2) Continuous derivatization and SPE pre-concentration. Eluent: acetonitrile.	LC-DAD Column: Varian C_{18} 150 mm x 4.6 mm (5 µm). Mobile phase: acetonitrile in water.	Acetaldehyde 0.3 µg/l, formaldehyde 1.0 µg/l	Linearity range (µg/l for a sample volume of 15 ml): Acetaldehyde 1-200, formaldehyde 3.5-200 with r^2>0.997.	Low maturity: Article (Banos & Silva 2009b)
water	Acetaldehyde, (and other aldehydes)	Q	In situ derivatization on SPE cartridges LiChrolut EN (particle size 40 – 120 µm, surface area ca. 1200 m^2/g)	LC-MS/MS Column: Varian Polaris 3 µm 150 mm x 2.0 mm RP-C_{18} Mobile phase: Solvent A: acetonitrile and MeOH, solvent B formic acid 0.1%	Acetaldehyde 18 ng/l	Linearity range for a 20 ml sample volume (µg/l) 0.06 – 15 (r^2 = 0.9995).	Low maturity: Article (Banos &Silva 2009a)

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
aqueous, soil and waste samples	Acetaldehyde, formaldehyde (and other carbonyl compounds)	Q	The sample is buffered to pH 3 and derivatized with DNPH. Two possible extraction techniques: (1) Solid-phase extraction (SPE) with sorbent cartridges and elution with ethanol. (2) Liquid-Liquid Extraction (LLE) using methylene chloride followed by concentration and exchange with acetonitrile prior to HPLC.	HPLC-UV/Vis Column: 250 mm x 4.6 mm i.d. 5 µm particle size, C_{18} column, Zorbax or equivalent. Mobile phases: containing acetonitrile and water.	SPE: Acetaldehyde 43.7 µg/l, formaldehyde 6.2 µg/l, LLE: Acetaldehyde 110.2 µg/l, formaldehyde 23.2 µg/l	If only formaldehyde is studied, the aqueous sample should be buffered to pH 5 to minimize formaldehyde formation. Acetone and MeOH react with DNPH, therefore glassware should not be rinsed with these solvents. Formaldehyde contamination of DNPH is often encountered. Acetaldehyde is generated during the derivatization step if ethanol is present in the sample, impairing the measurement of acetaldehyde below 0.5 ppm. Linearity and applicability range: 50-1000 µg/l. Round test in 12 laboratories. A possible way to automatise this analytical method was suggesten in (Wu, White 1995).	High maturity: US EPA method 8315A. (EPA 1996c) Procedure 1.
drinking and natural water	Acetaldehyde, formaldehyde (low molecular weight carbonyl compounds)	Q	Derivatization with DNPH after sample collection.	HPLC-UV/Vis Column: C-18 reverse-phase column (Kanto Kagaku, RP-18GP 5 µm 4.6 mm i.d. x 150 mm length). Pre-concentration column: C-18 reverse-phase (Kanto Kagaku, RP-18GP 5 µm 4.6 mm i.d. x 5 mm length. Two mobile phases used.	1- 3 nM	15 % acetonitrile aqueous solution was pushed through the pre-concentration column to remove unreacted DNPH, that interferes with the detection of formaldehyde. Relative standard deviation: 2- 5 % for 20 nM standard solutions. The analysis of water containing heavy metals was performed successfully by means of a similar method (DNPH-HPLC-UV) in (Lin et al. 2009)	Low maturity: Article (Takeda et al. 2006)

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
water	Formaldehyde, acetaldehyde (carbonyl compounds)	Q	Derivatization with 4-N,N-dimethylamino-6-(4´-methoxy-1´-naphtyl)-1,3,5-triazine-2-hydrazine (DMNTH) or N-Methyl-4-N´,N´-dimethylamino-6-(4´-methoxy-1´-naphthyl)-1,3,5-triazine-2-hydrazine (MDMNTH).	HPLC-UV/Vis or -DAD. Column: Supelco Discovery RP-18, particle size 5 µm, pore size 200 Å, 150 mm x 4.6 mm and guiard column 20 mm x 4 mm. Mobile phase, DMNTH: acetonitrile and a mixture of water-triethylamine-acetic acid, MDMNTH: acetonitrile and a mixture of water-triethylamine-trifluoroacetic acid.	*DMNTH* UV/vis: formaldehyde $2.5\cdot10^{-7}$ mol/l acetaldehyde $2.5\cdot10^{-7}$ mol/l DAD: formaldehyde $1.0\cdot10^{-7}$ mol/l, acetaldehyde $5.0\cdot10^{-7}$ mol/l. *MDMNTH* UV/vis: formaldehyde $5.0\cdot10^{-6}$ mol/l acetaldehyde $2.5\cdot10^{-6}$ mol/l DAD: formaldehyde $5.0\cdot10^{-6}$ mol/l acetaldehyde $2.5\cdot10^{-7}$ mol/l	Focus on the determination of carbonyls in waters in presence of nitrite.	Low maturity: Article (Kempter & Karst 2000)
water, wine, aqueous matrices	Acetaldehyde, formaldehyde (aliphatic aldehydes)	Q	Filtration by means of a nitrocellulose membrane.	HPLC-PAD Column: Aminex HPX-87H BioRad column (300 mm x 7.8 mm i.d. packed with 9 µm spherical sulfonated polystyrene-divinylbenzene copolymer beads. Mobile phase: deoxygenated 50mM $HClO_4$. PAD with platinum working electrode in acidic medium. Ag/AgCl combined reference electrode and stainless steel auxiliary counter electrode.	acetaldehyde 0.9 µM, formaldehyde 0.5 µM	No derivatization procedure needed. Linear range (µM): acetaldehyde 1.4 - 200, formaldehyde 1.0 – 200. Analyte recovery: acetaldehyde 82 %, formaldehyde 90 %.	Low maturity: Article (Casella & Contursi 2005)

Matrix	Compound	Method type	Pre-treatment	Instrument	LOD	Characteristics (Pros/Cons)	Maturity/Ref
pool water	Acetaldehyde (formaldehyde, carbonyl disinfection by-products)	Q	Derivatization by DNPH after sample collection. Pre-concentration by SPE with Oasis HLB cartridges (200 mg adsorbents). Elution with acetonitrile.	HPLC-ESI-MS/MS Column: Xterra MS C_{18} 2.1 mm x 150 mm, 5 µm particles. Mobile phases: Ammonium acetate in water and ammonium acetate in acetonitrile.	acetaldehyde: LOD: 0.18 µg/l LOQ: 0.65 µg/l Measurements in the µg/l are possible without sample pre-concentration by SPE.	After pre-concentration by SPE the derivatives were stable for several weeks when stored in acetonitrile at 4°C in the dark. Linearity range: 0.1 – 15 µg/l.	Low maturity: Article (Zwiener & 2002)
rain water	Acetaldehyde, formaldehyde (other aldehydes)	Q	Derivatization with hydrazino benzene sulfonic acid.	CE-UV Capillaries: fused silica capillaries of 75 µm i.d. Capillaries total length 0.78 m (0.58 m to the detector).	acetaldehyde 3.0 µM, formaldehyde 0.75 µM	Advantages of CE compared to HPLC are its high separation power and speed, a weak point is the detection sensitivity with LODs higher usually of one or two orders of magnitude.	Low maturity: Article (work financially supported by the European Commission). (Asthana et al. 1998)

4.6 Analysis of ammonia

Ammonia has been determined from several water matrices. Some of the methods are presented above when describing the methods for alkyl amines and alkanol amines (Mishra et al. 2001, Price et al. 1992, Siddiqi & Pathania 2003 and Hui et al. 2010). Ammonia was also determined from air (dust particles) along with acetamide (Nilsson et al. 2002). Multiple determination methods for ammonia in air and atmospheric samples exist, such as GC-FID method (Yamamoto et al. 1994). Some standard methods for ammonia analysis are presented below.

- ISO 7108:1985 Ammonia solution for industrial use - Determination of ammonia content - Titrimetric method
- ISO 9455-9:1993 Soft soldering fluxes - Test methods - Part 9: Determination of ammonia content
- SFS-EN 12122 Chemicals used for treatment of water intended for human consumption. Ammonia solution
- SFS-EN 12126 Chemicals used for treatment of water intended for human consumption. Liquefied ammonia
- SFS-EN 14671 Characterization of sludges. Pre-treatment for the determination of extractable ammonia using 2 mol/l potassium chloride
- OSHA Method 164: Ammonia in Workplace Atmosphere
- OSHA Method 188: Ammonia in Workplace Atmospheres - Solid Sorbent
- NIOSH Method 6015: Ammonia
- NIOSH Method 6016: Ammonia by IC
- ASTM D1426 - 58 Standard Methods of Test for Ammonia in Industrial Water and Industrial Waste Water
- ASTM D7550 - 09 Standard Test Method for Determination of Ammonium, Alkali and Alkaline Earth Metals in Hydrogen and Other Cell Feed Gases by Ion Chromatography
- ASTM UOP959 - 98 Ammonium Determination in Aqueous Solutions by Ion Chromatography

5. RECOMMENDATIONS ON THE ANALYTICAL METHODS

The fully validated standard methods should be favoured in the method selection since they have already gone through a complex evaluation and are suspected to be more readily applicable for the intended purpose instead of for example article methods. The analysis of a complex mixture of volatile n-nitrosamines is best to be carried out by GC-TEA, MS or MS/MS or alternatively HPLC-TEA, MS or MS/MS. The analysis of a complex mixtures of non-volatile nitrosamines are performed by HPLC equipped with TEA, MS or MS/MS. Also Ultra Performance Liquid Chromatography (UPLC) should be taken into account since the higher sensitivity when compared to HPLC. Some trace amount nitrosamines, such as NDMA, require MS/MS or High Resolution MS (HRMS) detectors due to their short retention time, which allows them to potentially co-elute with other LMW substances. The most successful way to analyze a complex mixture of both volatile and non-volatile nitrosamines at trace levels seems therefore to be HPLC-MS or HPLC-MS/MS. Analysis of N-nitrosamines in water at trace level requires extraction and pre-concentration. In the case of nitrosamines, SPE is preferred instead of LLE due to the amines high polarity and solubility in water.

In the case of primary and secondary alkylamines, GC with MS techniques seems to be the best method of analysis both in aqueous and air matrices due to its superiority in selectivity and sensitivity. Derivatization has been used to overcome the difficulties connected to direct GC analysis of LMW primary and secondary aliphatic amines. Air mixtures containing primary, secondary and tertiary aliphatic amines have been successfully analyzed by HPLC-MS/MS. The available literature on the analysis of primary, secondary and tertiary aliphatic amines in aqueous matrices is scarce. GC-NPD methods were found. SPE was proven more efficient than LLE for sample extraction and pre-concentration also in the case of alkylamines.

LC is preferred instead of GC in the analysis of alkanolamines. HPLC coupled with MS, MS/MS or FL is the best instrument to analyze the solvent amines at trace levels in both water or air matrices. Derivatization has often been used for trace analysis of these compounds. GC-MS or GC-FID methods were used to analyze the solvent amines present in rich/lean amine solvent. GC-FID and HPLC-RID were the only found methods able to detect the solvent amines and their degradation products simultaneously in flue gas matrix.

The information on analytical methods for the determination of acetamide and formamide in the matrices of interest is scarce. Due to the low molecular weight of these compounds, LC methods may not be feasible. GC-MS is used for the analysis of VOCs both in air and water. UV and NPD detectors are also suitable in combination with GC.

Standard methods for the determination of aldehydes in air samples use pre-column derivatization with DNPH and HPLC analysis. The detectors used are MS, MS/MS or UV. DNPH-GC-MS has also been successfully used in fully validated methods for the aldehydes of interest. DNPH derivatization has been performed during sampling on solid support. An ozone trap should be used during sampling since ozone consumes DNPH and degrades the derivatives. Water samples should be pre-concentrated by SPE for trace analysis. DNPH-HPLC-MS (or MS/MS or UV) is the method of choice for water analysis. For ammonia analysis, GC with FID has been suitable among MS techniques (Yamamoto et al. 1994). Also IC has been successfully employed (standard methods, e.g. NIOSH 6016, ASTM D7550 - 09 and ASTM UOP959 - 98).

Most of the methods found during this literature survey were for quantitative analysis but many of the presented quantitative methods are suitable for group and screening methods also. However, for group analysis less sensitive methods for example titrimetric, colorimetric, voltametric, chemiluminescence and spectrophotometric methods could be used. Also chromatographic methods with lower sensitivity detectors (such as FID or RI) might be usable.

6. FURTHER WORK

According to this literature review, multiple analysis methods are available for the analysis of the amines and other related compounds of interest. However, mostly chromatographic methods with MS detectors are recommended for the quantitative analysis. The most suitable analysis method can not be selected by literature survey only, and the method applicability needs to be tested experimentally. The analysis method is not only the analytical part but also pretreatment of the samples have to be taken account. Thus, at the sub-task 5 the main analytical methods with pretreatment found within this literature review will be tested and the most suitable method will be selected. The attention will also be paid on group and screening methods but the work will be started with creating a selective quantitative method. During the sub-task 5 work the information of the available methods will be constantly updated. Also the sampling procedure (sub-task 2) will be considered along with the analysis method developement.

Since the matrices for the analysis are very distinct from each other, different pretreatment methods could be needed even though the analysis would be performed in the similar manner. However, the sampling method plays an important role in the whole system and it might be possible to select the sampling method in a way that the pretreatment and analysis for flue gas and wash water sample can be performed more or less similarly. With the rich/lean amine solvent the same analytical methods as for wash water could be usable. Different pretreatment or separation of the solvent amines from the sample might also be needed but this needs further testing before anything detailed can be said of the procedure.

7. CONCLUSIONS

The scope of this literature research was to present analytical methods for solvent amines and their degradation products in CO_2-capture units. Aqueous solutions of various amines, in particular alkanolamines, are used as solvent in the absorber units of gas sweetening plants. The use of similar units to capture CO_2 from large point sources is a new application of the amine-absorption technology and a possible way to reduce the impact of CO_2 as a green house gas.

Several components with possible environmental impact have been identified among the products of degradation of solvent amines. N-nitrosamines and LMW alkylamines were the main focus of this literature research. Analytical methods for solvent amines, LMW amides and aldehydes were also studied. The matrices of interest were the treated flue gas from the absorber column (flue gas), the wash water from the absorber top (wash water) and the rich and lean aqueous amine solution circulating in the absorber (rich/lean amine solvent). All the compounds of interest were treated as trace compounds.

Majority of the methods found were from articles but many standard analysis methods were also available. Applying the method for analysis depends on the sample matrix. For example methods for the water can be easily applied for the wash water matrix but more work might be needed for detecting trace amounts of compounds in rich/lean amine solvent matrix. The method maturity, i.e. if the method is article based and not evaluated by others (low maturity) or if the method is a fully validated standard method (high maturity), was evaluated. The validated standard methods were assumed to be more readily applicable for the intended purposes since they have already gone through a complex evaluation. However, the methods available for example work place measurements are not necessary relevant for the stack sampling purposes.

The main conclusions and assumption made were the following:

- Analytical methods developed for air were considered to be mostly suitable for flue gas analysis but sampling method (sub-task 2) plays an important role
- Methods for water were assumed to be applied for wash water with the compounds of interest present on a trace level
- Rich/lean amine solvent matrix was more complex and there was only some information found in the literature related to analysis of trace amounts of other amines and compounds of interest from the solvent matrix
- The methods to be developed for water and/or gas analysis might be possible to be applied for solvent matrix as well
- Separation of solvent amines from rich/lean solvent matrix might be needed prior to analysis of trace amounts of other compounds. At least some pretreatment is expected to be needed
- Information is available on the analysis of the solvent amines, which are present in considerable amounts in rich/lean amine solvent
- Chromatographic methods, in particular GC and LC methods equipped or coupled with suitable detectors i.e. mass spectrometer (MS), tandem MS (MS/MS) or high resolution MS (HRMS), were found to be the most suitable methods for the analysis of the compound of interest at trace levels in both air and aqueous matrices. The same methods might be applied for rich/lean solvent amine matrix also
- The above mentioned methods apply mainly for quantitative and also for screening method. For group analysis, less sensitive methods can be used

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