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SINTEF REPORT

TITLE

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

Subtask 4: Literature survey of analytical procedures and recommendations

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ABSTRACT

The objective of H&ETQP/Amine1 is to have well documented analytical procedures for potentially harmful components from post combustion amine based CO2 capture to enable complete emission characterization.
The scope of work of Subtask 4 is to conduct a literature study that gives an overview over existing analytical methods, where the following should be given for each method: Applicability, main principle, instrumentation, detection limit, maturity, pros / cons and recommendations for further work. The study should cover the following compounds / groups of compounds: Amines, ammonia, aldehydes, amides, alkylamines and nitrosamines, and the following matrices: Treated flue gas, wash water from absorber and rich and lean amine solvent.
The following conclusions have been made: 1) standard methods exist mainly for work place air, ambient air and drinking water measurements, and have not been found for amine related analysis in emission characterization and monitoring, 2) For the amines, ammonia and alkylamines, mass spectrometric methodology has been established and applied to matrices relevant for this scope. 3) For aldehydes, amides and nitrosamines, there is a need to perform further method developments, validations and interference- and stability studies, based on mass spectrometric methodology. 4) The analytical methods for emission characterization should be based on modern mass spectrometric methodology, as a common generic methodological principle, that holds a quality in accordance with standards and guidelines used within other fields of analytical chemistry, like forensics and food chemistry.
It is recommended that: 1) Mass spectrometric methodology should be developed and validated to replace older methodology for all compounds or groups of compounds within the scope of this project. 2) The mass spectrometric methodology should be adapted to improved sampling methodology capable of trapping the groups of analytes in the scope, preferably by a common generic method.

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

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1 Background

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

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

2 Objectives

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

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

3 Scope of work

Literature survey of analytical procedures and recommendations

A literature survey shall be conducted which should give an overview over existing analytical methods, where the following should be given for each method:

- Applicability (for the various sample types)
- Main principle
- Instrumentation
- Detection limit
- Maturity (e.g. accredited method at contract laboratories/standard method, but less used/publication - need confirmation or development)
- Pros/cons
- Recommendations, included:
  - ranking of the methods
  - is the best ranked method satisfactory for the needs?
  - if not; suggest further work

The following groups of parameters apply for this study:

- amines, included emitted amounts of the specific solvent in use
- ammonia
- aldehydes
- amides
- alkylamines
- N-nitrosamines

The following sample types (matrices) apply for this study:

- Treated flue gas
- Wash water from absorber
- Rich and lean amine/solvent

4 Methods

In Subtask 4 the work has been based on available literature, standard methods and/or in-house developments. Specific search has been performed in databases available at SINTEF and on the Internet. Likewise, relevant standards have been searched for and the relevance of found standards have been checked.

5 Results

Six classes of compounds / compounds (amines, ammonia, aldehydes, amides, alkylamines and N-nitrosamines) listed in the scope of work have been examined in this literature study. The results form the study are tabulated in Appendices A to F. The tables contain found information about applicability, main principle, instrumentation, detection limit, maturity, pros / cons and ranking of the methods. Conclusions are given in chapter 5 and recommendations are given in chapter 6.

For each class of compounds, supplementary information and comments to the tables in Appendices A to F is given below in this chapter.

Standard methods and publications found relevant for the scope of this study are listed in references 1-53 (Section 9, References). Standard methods found to be relevant for this study, are also tabulated in Appendix G with additional information.

Appendix H gives a formula that can be used to calculate limit of detection by instrumental analysis to limits of detection in a flue gas sample.

5.1 Amines

Few standards methods for “amines” have been found (1-3). The information requested in the scope of work is tabulated in Appendix A for groups of amines and for single amine compounds.

For the class of amines it should be distinguished between ordinary amines and alkanolamines which differ from the amines by having one or more hydroxyl group in addition to the amine function. The alkanolamines are more polar than the amines, and unlike the ordinary amines, it is not possible to reduce the water solubility completely by a raise of the pH, e.g. for solvent extraction and sample preparation. This difference in polarity will, to a certain extent, influence on the applicability of some methodologies. Solvent amines can be both alkanolamines (like MEA) and amines (like piperazine) (52).

The amines can be analyzed by several methodologies. The least sophisticated methodologies are titration and colorimetric methods. By titration, the amines are measured as pH after stepwise addition of acid. The colorimetric methods are methods where the amine function undergoes a reaction which leads to formation of a product (a chromophore) that can be analyzed by a colorimetric method. The colorimetric methods are normally used without a chromatographic separation step. In such cases, and as with titration, the method will be very unspecific and not allow for measurement of two or more amines in combination, and besides, the method will be biased by co-determination of degradation products that also are amines (40).

Amines have also been analyzed by ion chromatography (IC). By IC the amines are separated on a cation exchange column while being eluted by a gradient of increasing concentrations of another cation. The most frequent way of detecting the amines in IC, is by conductimetric/electrochemical detection (EC). EC has little specificity, and the differentiations between different amines (and other cations) solely relay on the chromatographic retention times of the analytes, and that none of the analytes co-elute together with other amines or other cations. Recently, IC has been coupled to mass spectrometry (MS). MS gives high specificity to IC, however, IC-MS has not yet gained widespread use in amine analysis, so it is difficult to evaluate the applicability of this methodology (52).

Gas chromatography is well proven for analysis of amines, and different detectors have been applied. MS is probably the most preferable detection principle as this gives a high specificity and a high qualitative reliability. One challenge by GC has been to achieve good chromatographic properties for the most polar amines, and especially the alkanolamines. Polar compounds are prone to give poor peak shapes with tailing, and some amines react with the stationary phase of the columns. However, modern fused silica columns made especially for amines have to some extent eliminated this problem (52).

GC-MS has become a very useful instrumentation for identification and quantification of amines and amine degradation products. Operated in the scan mode, unknown amines can be identified by spectrum database search. Most GC-MS instruments are equipped with a spectrum data base that contains spectra of about 200 000 compounds. If the compound that is to be identified is in the spectrum database, it can be identified by a spectrum match. If the unknown compound is not in the spectrum database, it can not be identified this way, and more sophisticated methodology and competence is needed (52).

The normal way of utilizing a GC-MS instrument in amine analysis, is to run the MS in the SIM (selected ion monitoring) mode. In the SIM mode 2 to 3 characteristic masses are chosen that are unique for the amine of interest. Of the 2 to 3 signals monitored, one (the target ion) is used for quantification, while the two others (the qualifier ions) are used to verify the identity of the amine. This is possible because there will be a certain and reproducible response ratio given between the SIM signals for a compound. If the correct ratio is not found during analysis of unknown samples, it indicates that the analyte not has been correctly identified. The principle that ion ratios are demanded to be within certain predetermined limits (a limit of +/- 20% is often applied) is a central part of widely accepted guidelines that are used e.g. within forensic chemistry and doping (52).

Operated in the SIM mode, virtually all amines can be detected by GC-MS, the detection limits will normally be in the microgram per L range by direct injection. This sensitivity is more than sufficient for the control of solvents, but probably too low for control of water wash solutions and emission measurements, provided that normal sampling volumes of flue gas are used. It should be noted that the sensitivity of GC-MS can be radically enhanced by specialized techniques. Important examples are derivatization of a compound and concentrating of the analyte by sample preparation. In some cases, these techniques can enhance the sensitivity by a factor of more than one thousand (52).

The analytical technique that gives the highest performance qualitatively and quantitatively is LC-MS (liquid chromatography coupled with mass spectrometry). The very water soluble amines are well handled by LC, without derivatization, and the MS provides a high specificity. Due to the fact that most of the amines are easily ionized, the sensitivity is higher than with GC-MS. MS can be performed by single quadrupole MS (MS-SQ) or preferably with triple quadrupole technology (MS-QQQ). MS-QQQ gives strongly enhanced confidence with respect to the identification because the analyte molecule is fragmented and most compounds have unique fragmentation patterns and different daughter ions (which gives unique and compound-specific transitions). Because of the transition, the noise level is reduced, and an improved signal-to-noise ratio is achieved. Compared to MS-SQ, MS-QQQ gives on average ten times better sensitivity. And compared to GC-MS, the sensitivity of MS-QQQ is about one hundred to one thousand times better. This means that the detection limits are in the nanogram or sub-microgram per L range for LC-MS-QQQ. For samples of emitted flue gas, this sensitivity translates into the ppbv range (given an average molecular weight of 100 Dalton), by direct injection, provided that an average sample volume is applied. LC-MS-QQQ can also be applied on water wash, by direct injection,

with the same nanogram per mL sensitivity. Applied on amine solvent samples, LC-MS-QQQ in fact requires a dilution before injection by monitoring of the solvent amines. This is due to the high sensitivity, and the sensitivity is sufficient to monitor also important degradation products in the amine solvent (52).

SINTEF has developed LC-MS-QQQ methodology for numerous amines (and degradation products) (53). The amines are listed in Appendix A.

5.2 Ammonia

Standard methods for ammonia have been found (4-11). The information requested in the scope of work is tabulated in Appendix B for ammonia.

For ammonia, different methods have been used historically as titration, potentiometric (ion selective electrode) (6) and colorimetric methods (5, 7). Common for these methods is that they are unspecific, and can not be used when other amines are present. IC has been used (8), and is still used, in many laboratories that work with amine related carbon capture (52). All these methods are still in use in university laboratories that perform research in this field (52). Methods without separation like titration and colorimetric methods, like the indophenol blue method, are not suited for analysis of ammonia where other amines are likely to be present (40). IC methods, on the other hand, are currently being used for ammonia detected as $NH4^+$. Both methods can be applied after absorption of ammonia from flue gas in dilute sulphuric acid solutions (52).

SINTEF has developed a method for analysis of low concentrations of ammonia in aqueous solutions by GC-MS (53). This is the same method as the one described later for alkylamines. The method is based on direct derivatization of ammonia in aqueous solution. Derivatization can be performed directly on a sample taken from an absorption (or condensate) solution. The derivatization product has a much stronger MS response than underivatized ammonia, but with the high specificity of the MS. In addition, the product of the derivatization reaction gives a molecule with relatively low polarity that makes derivatized ammonia extractable from water with an organic solvent. Therefore, by extraction from larger volume of aqueous solution into a smaller volume of organic solvent (that can easily be further reduced by evaporation) allows for a concentrating step that can enhance the sensitivity for ammonia by GC-MS by a factor of one thousand (or more). Taken this possibility into consideration, it should be possible to achieve instrument sensitivity in the nanogram or sub-microgram per L range. This low instrumental detection limit should make it possible to measure flue gas concentrations down to the very low ppbv range, given normal sampling conditions and volumes (52).

5.3 Aldehydes

Standard methods for aldehydes have been found (12-25). The information requested in the scope of work is tabulated in Appendix C for groups of aldehydes and for single aldehyde (and carbonyl) compounds.

Aldehydes are reactive species that undergoes reactions with several other classes of compounds. Examples are reactions with water to form hemiacetals or acetals, with amines to form imines, with hydroxyl amines to form oximes, with semicarbazides to form semicarbazones and with hydrazines to form hydrazones. In addition, a large number of other reactions are possible due to the reactive carbonyl groups of the aldehydes (42).

In fact, the reactivity of the carbonyl group of aldehydes has been used for derivatization for analytical purposes, and to protect the aldehydes from unwanted reactions with other compounds. The most widely used derivatization method applied to the aldehydes is with dinitropehnylhydrazine (DNPH), and many standard methods are based on this principle. Derivatization with DNPH is also well described in the literature (42–49). The hydrazone formed after derivatization has UV-absorbing properties; therefore the most widespread instrumental analysis is liquid chromatography with UV-detector (LC-UV) (13, 15, 23). LC-UV gives good sensitivity (0.05 mg/L by direct injection), but low/medium specificity. With relatively low sampling volumes (6L) it is possible to achieve detection limits well below 1 ppm (2 mg/m3). This sensitivity can be strongly enhanced to the low ppb range. It should be emphasized that the standard methods referred to here are for ambient air / workplace monitoring, and not for flue gas with a high water content.

Three standard methods TO-11A, CARB 430 and EPA 8315A (Refs. 13, 15, 23) describe the direct derivatization with DNPH both in liquid (acidic) solution and with DNPH impregnated tubes. The impregnated tubes are of little relevance to the flue gas measurements; however, the impinger-based DNPH-methods should be transferable to measurements in flue gas from amine based carbon capture, although a standard for flue gas measurement not has been found.

The standard for measurement of aldehydes in liquid and solid samples (8315A) should be applicable to waste water, whereas applicability to amine solvents is low due to high concentrations of solvent amines that are likely to react with DNPH (52).

From the standard 8315A it was found that unreacted aldehyde is stable for three days at 4ºC prior to derivatization, and for three days after derivatization. This is very interesting, because this stability will open up for sampling of unreacted aldehyde and subsequent derivatization with DNPH at the laboratory (52).

More recent publications (Schulte-Ladbeck and Richardson) (43, 48, 49) have shown that the DNPH hydrazone derivatives also can be analyzed by LC-MS. Although the documentation is limited, this will open for a more specific and probably more sensitive instrumental methodology

than LC-MS. This possibility should be further investigated. It should be noted that DNPH also to some extent reacts with the carbonyl groups of ketones, and derivatives may be formed that may give chromatographic interferences with the LC-UV method. The risk for such interferences is eliminated with LC-MS (52).

DNPH derivatives has also been applied to GC-MS analysis and compared with dervatization with PFBOA (o-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (Sugaya) (45). This derivatization reagent forms carbonyl oximes with aldehydes. In this study, PFBOA was found to be superior to DNPH, although this difference is small. Head space injection may (generally) have relevance to solvent analysis because it is possible to avoid injection of large amounts of amine solvent.

PFBOA derivatization has also been applied to LC-MS with APCI ionization on emissions from diesel exhaust (Jakober) (47). In this study PFBOA derivatization enhanced the sensitivity compared to DNPH.

To conclude, the DNPH derivatization method is widely distributed in work-place and ambient air measurements. The sampling methodology with impinger trains can be modified and adapted to flue gas from amine based carbon capture. Although on-site direct derivatization with DNPH is possible, this is not a prerequisite and subsequent derivatization and processing is allowed (52). The enhanced specificity and sensitivity with LC-MS should be utilized, and the use of other derivatization reagents like PFBOA may further enhance both quality and sensitivity by LC-MS analysis. (44-46)

5.4 Amides

Standard methods for amides have been found (26-31). The information requested in the scope of work is tabulated in Appendix D for single amides.

The group “amides” is large since the amide function is widespread with a large and inhomogeneous inventory of compounds. Amides, in this context, are therefore mainly considered as the low molecular reaction products of amines with different acids.

Formamide and acetamide has been measured as work-place contaminants after adsorption to silica gel (OSHA) (30, 31). In these procedures analysis has been performed by gas chromatography with FID (formamide) and NPD (acetamide). The gas chromatographic performance is, however, of low quality with severe tailing (52).

Formamide and acetamide are both water soluble compounds that also would be possible to trap in impingers with aqueous solutions (52).

SINTEF has under development, methodology for formamide and acetamide based on LC-MS-QQQ. With this methodology, we analyze both compounds with an instrumental sensitivity of 10 ng/mL (52).

SINTEF has developed methodology for other amides that have been identified and have been considered to be of interest. Liquid chromatography with triplequadrupole mass spectrometry (LC-MS-QQQ) is the methodology that has given the best performance with respect to sensitivity and specificity for these compounds (52).

5.5 Alkylamines

One standard method for alkylamines have been found (32). The information requested in the scope of work is tabulated in Appendix E for single alkylamines.

The standard method for work-place measurement describes the analysis of the alkylamine diethylamine. The standard describes absorption on silica gel tube and subsequent analysis by GC-FID (32).

Due to their high polarity, the alkylamines can be analyzed by IC-EI by the same principle as ammonia. A possible interference by determination of alkylamines with IC-EC is the presence of large amounts of ammonia (52).

Due to their low molecular weights, the alkylamines have relatively poor detection limits both with GC-FID and by GC-MS. This is also valid for analysis of low-molecular weight compounds by LC-MS (52).

SINTEF has developed a derivatization method that helps to overcome the lack of response for the alkylamines (this is the same method that is used for ammonia above). The derivatives of the alkylamines have an increased response by GC-MS that allows detection with an instrumental sensitivity of < 10 µg/L by direct injection. Moreover, the derivatives formed are less polar than the alkylamines and they can therefore be extracted from an aqueous water phase into an organic solvent phase with a lower volume, and thereby be concentrated. The solvent extract can be further reduced in volume, and the sample can therefore be more concentrated. Due to these processes, a concentrating factor of more than one thousand can be achieved (53).

5.6 Nitrosamines

Standard methods for nitrosamines have been found (33-39). The information requested in the scope of work is tabulated in Appendix F for nitrosamines as group and as single nitrosamines.

The existing methodologies and standard methods for sampling and analysis of nitrosamines are influenced by the fact that the focus on nitrosamine toxicity has been changing with time. Examples are nitrosamines in food, at work place (rubber industry, cutting oils), in cigarette smoke, drinking water etc.

Many of the standard methods found for analysis of nitrosamines uses absorption on Thermosorb/N tubes in combination with the TEA analyzer (Thermal Energy Analyzer). The Thermosorb/N tube does not tolerate water well (a maximum of 75L is recommended at 80% relative humidity at 22ºC (approx. 10 g water per m^3)), so this sampling device has limited relevance and applicability for sampling of nitrosamines in saturated flue gas at 50ºC (approx. 95 g water per m^3). It is, in principle, possible to reduce the water content of the flue gas with a cold trap and have a Thermosorb/N tube mounted downstream to the cold trap; however, it is a substantial risk of loss of analytes in the cold trap (52).

The TEA analyzer is "nitrosamine-specific" and the principle behind, is that at a certain temperature, the nitroso-function of the nitrosamine will be splitted off as NO. NO is converted to an electronically exited nitrogen dioxide which then decays back to NO_2 while light is being emitted, and the emitted light can be detected by chemiluminescence. The NCD (Nitrogen Chemiluminescence Detector) is a further development of the TEA that has higher sensitivity and better stability. The NCD detector is (as the TEA) normally coupled to a GC (52).

The GC-NCD detector is very interesting due to its possibility to screen for unknown nitrosamines, and SINTEF has developed a GC-MS-NCD method that combines the nitrosamine-specificty of the NCD detector with the identification power of the MS (53).

For specific detection of dedicated nitrosamines with the highest possible sensitivity, the LC-MS-QQQ methodology performs best. SINTEF has up to now developed LC-MS-QQQ methodology for 10 different nitrosamines as shown in Appendix F. With this methodology it is possible to detect most nitrosamines with an instrumental sensitivity between 0.1 and 10 µg/L (53).

6 Discussion

6.1 Matrix effects

The different types of matrices that apply for this study are, treated flue gas, wash water from absorber and rich / lean amine solvent. It should be emphasized that determination of the one and same compound in these different matrices with the same method principle, can be extremely challenging and may require specific adaptations of the methods (52).

6.2 Amine solvents

The analysis of minor compounds (in microgram per L (ppb) concentrations) in amine solvents (with up to 5-6 mol/L concentration) may be complicated due to a massive interference from the amine solvent itself. In challenging situations like this, different strategies may be applied to the

sample before instrumental analysis. One strategy is to perform a sample preparation that removes the majority of the dominating compounds (the amines) prior to analysis, i.e. to remove the compound from the matrix by *extraction*. Extraction, however, can be extremely difficult if the compound of interest has chemical properties very similar to the interfering amines (e.g. removal of one amine (degradation product) from the amine solvent would typically be difficult. It should also be noted that the amine solvents themselves are strong bases. The injection of strong bases may give damage to instrumental equipment (especially chromatographic columns). An alternative to extraction is therefore to dilute the solvent sample before injection to remove this problem. This is possible if a method has very high instrumental sensitivity. A dilution of one hundred times will eliminate most solvent related problems, and still give a sufficient sensitivity. The instrument that has the highest sensitivity is LC-MS-QQQ, and with this instrument the dilution strategy has proven to be very useful (52).

6.3 Wash water from absorber

As a matrix, wash water is less challenging than the amine solvents. This is because wash water mainly consist of water without high concentrations of interfering compounds. For analysis in wash water the main challenge would be sensitivity and complexity. Numerous degradation products are formed within the absorber / stripper parts of the amine system, and many of these could enter the wash water. Here the methodology should have the highest possible sensitivity. Normally, wash water can be directly injected to an LC-MS-QQQ instrument, giving the highest achievable sensitivity for most analytes within the scope of this subtask (52).

6.4 Treated flue gas

To be *analyzed*, by the methodologies that fall within the scope of this project, a compound in flue gas needs to be *captured*. In practice, this means be absorbed into a liquid absorption solution or adsorbed onto a solid adsorbent tube. The liquid absorption solution can normally be injected directly onto an analytical instrument (normally GC or LC). Analytes adsorbed on a solid adsorbent tube need to be desorbed by elution with a solvent prior to injection. There is (presently) is *no standardized way of capturing the analytes from flue gas that are applicable to a broad spectrum of compounds of different classes* at the same time. This refers to the classes of compounds that are listed in the scope of this project, and there are other classes of compounds in addition to the classes listed, that also would be challenging to capture. Examples are the organic acids (together with amine bases) and certain ionic species like nitrite/nitrate.

Regardless of the sampling methodology, it is crucial to ensure that the chemical *stability* of the analytes is ensured both *during* and after *sampling*. Many of the compounds that are likely to be found in flue gas are *reactive species*. Well-known examples are the reactions of the aldehydes with several groups of compounds, and the reactions of secondary amines with nitrite (and related species) that may lead to the formation of nitrosamines. It is therefore extremely important that it

is focused on the *medium* that the analytes are *absorbed into* (or adsorbed onto), and the medium that the analytes a *stored in* after sampling.

For most reactions and compounds, the reactivity can be altered by correct selection of the pH value of the medium. However, there is no common pH that protects against unwanted reactions for a broad range of compounds. For example, the reactions between secondary amines and nitrite seem to have different *pH optima* (50). For this reaction, the anti-nitrosating effects of *nitrite scavengers* like ascorbic acid and sulfamic acid has been documented (51).

Instant freezing and storing of the media on liquid nitrogen (at minus 196ºC) seems to be a possible way of *sample preservation* prior to analysis. The efficacy of this extremely low temperature on stability has not been found studied or documented in the literature, neither for the prevention of nitrosation nor other unwanted reactions. Since freezing and storing on liquid nitrogen is a well-known and standardized method for preservation of biological samples for analysis (of a vast number of biological analytes), this preservation method may have a potential as *a generic preservation method* also for amine related samples (52).

If the analytes captured from treated flue gas are stored in a dilute aqueous medium, containing low concentrations of additives/other chemicals, this medium would be well suited for direct injection and analysis with LC-MS-MS-QQQ, as for wash water samples described above. LC-MS-MS-QQQ methodology currently represents the most *versatile* and *flexible* method for analysis of the majority of amine-related compounds encountered in flue gas (52).

6.5 Analytical methods / characteristics

Measurement of low concentrations of analytes (in a complex mixture) in strong amine solvents can be performed if the analytical method of choice has a very high *specificity*, in combination with a high *sensitivity*. Specificity is defined as the ability of one compound to be analyzed without interference from the other compounds in the sample. Specificity can be achieved by a *chromatographic* separation step included in the instrumental methodology. Thus, separation of the analyte from a major solvent peak may solve the problem of interference if the compounds are eluted from the column with a sufficient distance in time (52).

Another way of achieving specificity is if an analyte possesses specific (unique) properties with respect to the *detection principle*. Examples of detectors with such uniqueness could be TEA, fluorescence, UV absorption, detectors with specific or high sensitivity for certain elements (nitrogen, sulphur, metals etc.). Such more or less specific detectors are available both for gas chromatographic and liquid chromatographic techniques (52).

The most specific detection principle of all, that is applicable to a very large number of different analytes, is without doubt *mass spectrometry* (MS). With MS it is possible to detect an analyte on the basis of its *molecular weight* and on the basis of *specific (unique) fragmentation patterns*. MS has during the last two decades gained widespread use within most fields of analytical chemistry,

and has become the “gold standard” within fields where the demands for secure identification qualitatively and high sensitivity quantitatively are the highest (52).

A desired property for an analytical procedure (and for a sampling procedure) is *versatility*. This means that one methodology can be used for a range of different compounds. It is also desirable that the methodology in addition is *generic* or *flexible*, which means that the methodology is easily adaptable to new compounds that one would wish to include in the analysis (52).

As seen from the Appendices A to G, *mass spectrometry* has proven to be both *highly specific* and *very sensitive* for a large number of analytes belonging to all groups of compounds within the scope of this project. For two groups of analytes, the aldehydes and the alkylamines, derivatization prior to analysis may be favourable. For the aldehydes, this is especially important because derivatization enhances stability, but also because it increases sensitivity. For the alkylamines the major advantage with derivatization is the increased sensitivity, because the sensitivity is somewhat poorer with LC-MS-MS-QQQ for very small molecules like ammonia and methylamine. For all other groups of analytes, the analytical performance is good with LC-MS-MS-QQQ (52).

It is expected that the sensitivity of the LC-MS-MS-QQQ methodology will be increased, from the levels that are given in the Appendices, by a factor of 10 with the next generation of LC-MS-MS-QQQ instruments. This increase in sensitivity will be very valuable and beneficial for emission measurements in treated flue gas. The improved LC-MS-MS-QQQ technology with enhanced sensitivity will be available in the very near future (52).

7 Conclusions

The following conclusions can be drawn:

1) Standard methods for the compounds within this scope exist mainly for work place air, ambient air and drinking water measurements, and have not been found for amine related analysis in emission characterization and monitoring
2) For the amines, ammonia and alkylamines, mass spectrometric methodology has been established and applied to matrices relevant for this scope
3) For aldehydes, amides and nitrosamines, there is a need to perform further method developments, validations and interference- and stability studies, based on mass spectrometric methodology
4) The analytical methods for emission characterization should be based on modern mass spectrometric methodology, as a common generic methodological principle, that holds a quality in accordance with standards and guidelines used within other fields of analytical chemistry, like forensics and food chemistry

Table 1 summarizes our recommendations for analytical methodologies for the compounds of interest listed in Appendix A-F:

Table 1 Summary of recommended methodologies

Analytes	**Methodology**	**Rank**	**Satis-factory**	**Comments**
Amines	LC-MS-MS-QQQ	1	Yes	None
Ammonia	GC-MS	1	Yes	None
Aldehydes	LC-MS-MS-QQQ	1	No	Further development needed (see below)
Amides	LC-MS-MS-QQQ	1	No	Further development needed (see below)
Alkylamines	GC-MS	1	Yes	None
Nitrosamines	LC-MS-MS-QQQ	1	No	Further development needed (Subtask 5)

8 Recommendations for further work

It is recommended that:

1) Mass spectrometric methodology should be developed and validated to replace older methodology for all compounds or groups of compounds within the scope of this project.
2) New mass spectrometric methodology should be adapted to improved sampling methodology capable of trapping the groups of analytes in the scope, preferably with a common generic method.

Specific recommendations given:

8.1 Aldehydes

Aldehydes has been analyzed after derivatization with DNPH. This principle seems to work well both with LC-UV and LC-MS (Refs. 43, 48, 49).

The DNPH derivatization method in combination with LC-MS-MS-QQQ should be the selected methodology for further validation and testing.

The stability of selected aldehydes should be investigated in different matrices (solvents, wash water and flue gas samples).

The stability should be investigated both as underivatized and DNPH-derivatized compounds.

The possibility for a concentrating step based on solvent extraction should be verified.

Aldehydes other than formaldehyde and acetaldehyde should be considered.

As an alternative to DNPH, two other derivatization reagents (PFBOA and 4-APEBA) should be considered and eventually further elucidated by simple experiments. PFBOA may give increased sensitivity for aldehydes with GC-MS-NCI (46). 4-APEBA has the advantage that it will react also with carboxylic acids (44). This reagent was recently (in 2010) suggested as favourable for the combined LC-MS analysis of aldehydes and carboxylic acids. Carboxylic acids are an important part of amine chemistry, and are important for the understanding of amine degradation and the calculation of mass balances. Carboxylic acids normally require IC instrumentation for analysis. IC is less specific and more time consuming than LC-MS.

8.2 Amides

Preliminary in-house results have shown that amides (formamide and acetamide) can be analyzed directly by LC-MS-MS-QQQ. Other relevant aldehydes have also proved to be efficiently analyzad by LC-MS-MS-QQQ.

The analysis of selected amides (including formamide and acetamide) with LC-MS-MS-QQQ methodology should be tested further. If promising with respect to specificity and sensitivity, this methodology should be validated and tested.

The stability of selected amides should be investigated in different matrices (solvents, wash water and flue gas samples).

8.3 Adaptation of analytical methodology to sampling methodology

The LC-MS-MS-QQQ methods for aldehydes and amides should be adapted to relevant absorption media determined as part of Subtask 2.

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35) Volatile nitrosamine mixture 2 (NMEA, NDiPA, NMBA, NEBA, NBPA, NDAmA), OSHA, #38
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10 Abbreviations used in text or Appendices

S =	Amine solvent
WW =	Wash water
FG =	Flue gas
WA =	Work place air
GC =	Gas chromatography
MS =	Mass spectrometry
GC-FID =	Gas chromatography with flame ionization detection
GC-MS =	Gas chromatography with mass spectrometric detection
GC-NCD =	Gas chromatography with nitrogen chemiluminescence detection
GC-NPD =	Gas chromatography with nitrogen phosphorous detection
LC =	Liquid chromatogtaphy
LC-UV =	Liquid chromatography with ultraviolet detection
LC-MS =	Liquid chromatography with mass spectrometric detection
LC-MS-QQQ	Liquid chromatography with triplequadrupole mass spectrometric detection

EPA =	Environmental Protection Agency
NIOSH =	National Institute for Occupational Safety and Health
OSHA =	Occupational Safety and Helath Administration
NCASI =	National Council for Air and Stream Improvement
CARB =	California Environmental Protection Agency
APHA =	American Public Health Association

APPENDIX A - AMINES

Compounds	Applicability (S/WW/FG/WA)	Main principle	Instrumen-tation	LOD	Maturity	Pros	Cons	Ranking
"Amines" (Ref. 52)	S/WW/FG	Ion Chromatography with conductivity or electrochemical detection	IC-EC	Medium sensitivity	High	Very polar amines can be handled. Concentrated amine solutions affects retention times in cation mode	Unspecific. Long runtimes, up to 1 hour per sample. Strong solvent concentrations affect chromatographic performance and retention times negatively.	5
"Amines" (Ref. 52)	S/WW/FG	Ion Chromatography with MS detection	IC-MS	Medium sensitivity	Low	Very polar amines can be handled. Concentrated amine solutions affects retention times in cation mode	Highly specific. Faster throughput due to MS detection, overlapping peaks can be accepted.	4
"Amines" (Ref. 2)	S/ WW	Gas chromatography with FID detection	GC-FID	Gram to milligram per L	Medium	Robust detection principle	Unspecific detection principle	6
"Amines" (Ref. 53)	S/WW/FG	Gas chromatography with MS detection	GC-MS	Milligram and sub-milligram per L	High	Versatile and specific detection principle allowing specific and sensitive detection of amines	None	3

"Amines" (Ref. 53)	S/WW	Liquid chromatography with UV detection	LC-UV	Poor sensitivity	Medium	Low sensitivity	Unspecific detection principle, poor sensitivity	7
"Amines" (Ref. 52)	S/WW/FG	Liquid chromatography with UV detection after derivatization with naphthylthio-isocyanate (NITC)	LC-UV	High sensitivity	Medium	High sensitivity	Unspecific detection principle	6
"Amines" (Ref. 53)	S/WW/FG	Liquid chromatography with MS detection	LC-MS	High sensitivity	Medium / high	Versatile and specific detection principle allowing specific and sensitive detection of amines		2
"Amines" (Ref. 53) (For details, see Appendix I)	S/WW/FG	Liquid chromatography with triplequadrupole MS detection	LC-MS-QQQ	Very high sensitivity	Medium / high	Versatile and specific detection principle allowing specific and very sensitive detection of amines		1

APPENDIX B - AMMONIA

Compounds	Applicability (S/WW/FG/ WA)	Main principle	Instrumen-tation	LOD	Maturity	Pros	Cons	Ranking
Ammonia (Refs. 5, 7)	WW/FG	Colorimetric (indophenol)	Spectro-photometer	FG: 0.1 to 20 mg/m3	High		Unspecific. Interference from high concentrations of other amines. Sulphide interferes	3
Ammonia (Ref. 6)	WW	Potentiometric	Ion selective electrode	FG: 30 mg/m3	Low		Interferences from other volatile amines	4
Ammonia (Ref. 8)	S/WW/FG	Ion chromatography	IC-EI	FG: 17 mg/m3 (30 L)	High		Interferences from other amines likely (alkylamines)	2
Ammonia (Ref. 53) (For details, see Appendix J)	WW/FG	Gas chromatography after derivatization	GC-MS	FG: 0.1 mg/m3	Low	High specificity and high sensitivity	The need for derivatization	1

APPENDIX C - ALDEHYDES

Compounds	Applicability (S/WW/FG/WA)	Main principle	Instrumen-tation	LOD	Maturity	Pros	Cons	Ranking
Aldehydes (Ref. 13, 15, 23)	WW/FG/WA	Derivatization with dinitrophenyl hydrazine (DNPH) to form hydrazones	LC-UV	Air: Low ppb range WW: 50 µg/L	High (for sampling), medium for analysis	Well established principle	Low sensitivity, not validated for amine based carbon capture.	2
Aldehydes (Ref. 43, 48, 49)	WW/FG	Derivatization with dinitrophenyl hydrazine (DNPH) to form hydrazones	LC-MS		Low	Well established principle. Possible to distinguish aldehydes from ketones.	High sensitivity, not validated for workplace/ambient or amine based carbon capture.	1
Aldehydes (Ref. 52)	Water	Derivatization with dinitrophenyl hydrazine (DNPH) to form hydrazones	GC-MS with head space injection		Low		Not established, not tested	4
Aldehydes (Ref. 45)	Water	Derivatization with pentafluoro benzyl hydroxylamine (PFBOA) to form carbonyl oximes	GC-MS with head space injection		Low		Not established, not tested	5
Aldehydes (Ref. 47)	Diesel emissions	Derivatization with pentafluoro benzyl hydroxylamine (PFBOA) to form carbonyl oximes	LC-MS (APCI)		Low		Not established, not tested	3

APPENDIX D - AMIDES

Compounds	Applicability (S/WW/FG/WA)	Main principle	Instrumen-tation	LOD	Maturity	Pros	Cons	Ranking
Formamide (Ref. 30)	WW/FG	Gas chromatography	GC-FID	Milligrams per L	Low		Low sensitivity, low specificity, poor chromatography	3
Acetamide (Ref. 31)	WW/FG	Gas chromatography	GC-NPD GC-FID	10 mg/L	Low		Low sensitivity, low specificity, poor chromatography	2
Amides (Ref. 53) (For details, see Appendix K)	(S)/WW/FG	Liquid chromatography	LC-MS-QQQ	10µg/L	Low	High sensitivity, high specificity		1

APPENDIX E - ALKYLAMINES

Compounds	Applicability (S/WW/FG/WA)	Main principle	Instrumen-tation	LOD	Maturity	Pros	Cons	Ranking
Diethylamine (Ref. 32)	WA	Gas chromatography	GC-FID	Air: 7.5 mg/m3	Medium		Low sensitivity, low specificity	3
Alkylamines (Ref. 32)	S/WW/FG	Ion chromatography	IC-EI		Medium		Interference from ammonia very likely	2
Alkylamines (Ref. 53) (For details, see Appendix L)	WW/FG	Gas chromatography after derivatization	GC-MS	<10µg/L	Medium	High sensitivity, high specificity		1

APPENDIX F - NITROSAMINES

Compounds	Applicability (S/WW/FG/WA)	Main principle	Instrumen-tation	LOD	Maturity	Pros	Cons	Ranking
Nitrosamines (NDMA, NDEA, NDPA, NDBA, NPIP, NPYR, NMOR NMEA, NDiPA, NMBA, NEBA, NBPA, NDAmA) (Refs. 34, 35)	WA	Thermal Energy Analyzer (TEA) after absorption on Thermosorb/N (TM) tubes	GC-TEA	WA: 0.13 to 0.20 ug/m3 (with 75L air)	FG: Low/not applicable with Thermosorb tube due to interference with water	Well defined and validated method for workplace air (WA)	Not applicable to flue gas (FG) with Thermosorb tube due to interference with water	2
NDELA (Ref. 41)	WA	TEA after adsorption on impregnated filters or Thermosorb/N tubes and derivatization with N-methyl-N-trimethylsilyl-heptafluorobutyramide (MSHFBA)	GC-TEA	WA: 0.035 ug/m3 (with 2 m3 air, and impregnated filter)	FG: Low/ medium, not applicable with Thermosorb tube due to interference with water	Well defined and validated method for workplace air (WA)	Not applicable to flue gas (FG) with Thermosorb tube due to interference with water	2
Nitrosamines (Ref. 53) (For details, see Appendix M)	S/WW/FG	Liquid chromatography with triplequadrupole mass spectrometry	LC-MS-QQQ	S: <100 µg/L WW: <1 µg/L FG: <0.1 ug/m3 (with 1 m3 FG)	Medium	Sensitive and specific method		1

APPENDIX G – STANDARD METHODS

Compound /class	Method name	Matrix	Agency	Code
Amines	Aromatic amines	Air	NIOSH	2002
Amines	Aliphatic amines	Air	NIOSH	2010
Amines	Naphthylamines	Air	NIOSH	5518
Ammonia	Procedure for collection and analysis of ammonia in stationary sources	Air	EPA	206
Ammonia	Determination of ammonia nitrogen by semi-automated colorimetry	Water	EPA	350.1
Ammonia	Nitrogen, ammonia (Potentiometric, Ion selective electrode)	Water	EPA	350.3
Ammonia	Ammonia	Air	NIOSH	6015
Ammonia	Ammonia by IC	Air	NIOSH	6016
Ammonia	Procedure for collection and analysis of ammonia in stationary sources	Air	EPA	CTM-027
Ammonia	Ammonia	Air	OSHA	ID-188
Ammonia	Ammonia by selective electrode	Water	APHA	SM 4500-NH3 D
Aldehydes	Impinger source sampling method for selected aldehydes ketones and polar compounds	Air	NCASI	NCASI ISS/FP-A 105.01
Aldehydes	Aldehydes/ketones from DNPH adsorbents by HPLC	Air	EPA	TO-11A
Aldehydes	Determination of aldehydes/ketones in ambient air by HPLC	Air	EPA	TO-5
Aldehydes	Determination of carbonyl compounds by high performance liquid chromatography (HPLC)	Water	EPA	8315A
Formaldehyde	Formaldehyde by HPLC	Air	NIOSH	2016
Formaldehyde	Formaldehyde by GC/FID	Air	NIOSH	2541
Formaldehyde	Sampling and analysis for formaldehyde emissions from stationary sources in the mineral wool and wool fiberglass industries	Air	EPA	316
Formaldehyde	Measurement of formaldehyde emissions from natural gas-fired stationary sources. Acetyl acetone derivatization method	Air	EPA	323
Formaldehyde	Formaldehyde by visible absorption spectrophotometry	Air	NIOSH	3500
Formaldehyde	Acrolein and formaldehyde	Air	OSHA	52

Formaldehyde	Formaldehyde on dust (textile or wood)	Air	NIOSH	5700
Formaldehyde	Determination of formaldehyde and acetaldehyde in emissions from stationary sources	Air	CARB	CARB 430
Formaldehyde	Formaldehyde by colorimetric determination	Air	OSHA	ID-205
Formaldehyde	Chilled impinger method for use at wood products mills to measure formaldehyde, methanol and phenol	Air	NCASI	NCASI 98.01
Acetaldehyde	Acetaldehyde by GC/FID	Air	NIOSH	2538
Acetaldehyde	Acetaldehyde by GC/NPD	Air	OSHA	68
Acetaldehyde	Determination of formaldehyde and acetaldehyde in emissionsfrom stationary sources	Air	CARB	CARB 430
Acetaldehyde	Chilled impinger/silica gel tube test method at pulp mill sources for methanol, acetone, acetaldehyde, methyl ethyl ketone and formaldehyde	Air	NCASI	NCASI CI/SG/pulp 94.02
Amides	Dimethylacetamide	Air	NIOSH	2004
	Acrylamide	Air	OSHA	21
	N,N-Dimethylformamide	Air	OSHA	66
	Acrylamide	Air	OSHA	PV2004
	Formamide	Air	OSHA	
	Acetamide	Air	OSHA	PV2084
Alkylamines	Aliphatic amines	Air	NIOSH	2010
N-nitrosamines	Nitrosamines	Air	NIOSH	2522
N-nitrosamines	Volatile nitrosamine mixture 1 (NDMA, NDEA, NDPA, NDBA, NPIP, NPYR, NMOR)	Air	OSHA	#27
N-nitrosamines	Volatile nitrosamine mixture 2 (NMEA, NDiPA, NMBA, NEBA, NBPA, NDAmA)	Air	OSHA	#38
N-nitrosamines	Nitrosamines	Water	EPA	607
N-nitrosamines	Determination of nitrosamines in drinking water by solid phase extraction and capillary column gas chromatography with large volume injection and chemical ionization tandem mass spectrometry	Water	EPA	600/R-05/054

N-nitrosamines	Nitrosamines by gas chromatography	Water	EPA	8070A
N-nitrosamines	Nitroaromatics and nitramines by high performance liquid chromatography	Water	EPA	8330A

APPENDIX H – CALCULATIONS FROM INSTRUMENTAL LIMIT OF DETECTION TO FLUE GAS LIMIT OF DETECTION

Instrumental sensitivity: In tables given as ng/mL by direct incection (A)

Volume of liquid sample absorbed (or condensed) from the flue gas: Given as mL (B)

Volume of flue gas sampled: Given as m3 (C)

Sampling efficiency factor: 0.9 assuming a sampling efficiency of 90% (no data available, therefore a conservative efficiency for absorption / desorption is chosen)

$$\text{Limit of detection in flue gas sample (in ng/m3)} = \frac{\text{A (ng/mL)} * \text{B (mL)}}{0.9 * \text{C (m3)}}$$