CO_2 Capture Mongstad - Project A – Establishing sampling and analytical procedures for potentially harmful components from post-combustion amine based CO_2 capture

Task 3: Online Sampling and Analysis

K.W. Riley, A. Angove, B. Halliburton, A. Tibbett,
S. Sharma, M. Attalla and M. Azzi.

24th December, 2010.

EP105968

www.csiro.au

Enquiries should be addressed to:

Merched Azzi

Phone: 61 2 9490 5307

Email: merched.azzi@csiro.au

Copyright and Disclaimer

© 2010 CSIRO To the extent permitted by law, all rights are reserved and no part of this publication covered by copyright may be reproduced or copied in any form or by any means except with the written permission of CSIRO.

Important Disclaimer

CSIRO advises that the information contained in this publication comprises general statements based on scientific research. The reader is advised and needs to be aware that such information may be incomplete or unable to be used in any specific situation. No reliance or actions must therefore be made on that information without seeking prior expert professional, scientific and technical advice. To the extent permitted by law, CSIRO (including its employees and consultants) excludes all liability to any person for any consequences, including but not limited to all losses, damages, costs, expenses and any other compensation, arising directly or indirectly from using this publication (in part or in whole) and any information or material contained in it.

Contact Us
Phone: 1300 363 400
+61 3 9545 2176
Email: enquiries@csiro.au
Web: www.csiro.au

Your CSIRO

Australia is founding its future on science and innovation. Its national science agency, CSIRO, is a powerhouse of ideas, technologies and skills for building prosperity, growth, health and sustainability. It serves governments, industries, business and communities across the nation.

Report	**Version**	**Uploaded**
Project A Task 3	Draft	11th October
Project A Task 3	2nd Draft	10th November
Project A Task 3	Final	24th December

CONTENTS

EXECUTIVE SUMMARY 6

1 INTRODUCTION 8

2 ONLINE ANALYSERS 16

2.1 General 16

2.2 Chemiluminescence 17

2.3 Infrared Systems 18

2.4 Ultraviolet Systems 20

2.5 DOAS Systems 21

2.6 Flame Ionisation 22

2.7 Gas Chromatography 22

2.8 Mass Spectrometry 22

2.9 Ion Mobility Spectroscopy (IMS) 23

2.10 Photoacoustic Spectroscopy (PAS) 24

2.11 Further Research 25

3 PROS AND CONS OF COMMERCIALLY AVAILABLE ONLINE TECHNIQUES 26

3.1 Is drying possible? 26

3.2 Chemiluminescence 26

3.3 Infrared Systems 27

3.4 Ultraviolet Systems 27

3.5 DOAS Systems 27

3.6 Gas Chromotagraphy/Flame Ionisation 27

3.7 Mass Spectrometry 28

3.8 Ion Mobility Spectroscopy (IMS) 28

3.9 Photoacoustic Spectroscopy (PAS) 28

3.10 The Best System 29

4 CONCLUSIONS AND RECOMMENDATIONS.. 29

5 ACKNOWLEDGEMENTS 31

6 REFERENCES.. 31

APPENDIX: ANALYTES 36

- A.1 Aldehydes.. 36
- A.2 Amines (includes akylamines and alkanolamines).......................... 39
- A.3 Amides... 39
- A.4 Ammonia 40
- A.6 N-nitrosamines.. 41
- A.7 Bibliography for Appendix... 41

EXECUTIVE SUMMARY

Online Analysers will likely have a role in the control of amine-based post combustion capture (PCC) plants and maybe in the estimation of atmospheric emissions from such plants. But is unlikely that development of online systems directly applicable to such plants will not be fully developed before there are numbers of these plants in existence or before legislation is in place for the control of such plants. One of the limitations of online analysers is the relatively poor sensitivity achievable. The analytes of interest in this study are amines (including alkanolamines), their impurities and their degradation products i.e. ammonia, aldehydes, amides, alkylamines and N-nitrosamines. It is thought that the Norwegian authorities will mandate regulations to minimise the health and environmental impacts of amine emissions and these will have to be measured at a concentration of 0.01 to 0.1 ppmv as the Emission Limit Value (ELV) is likely to be 0.1 to 1 ppmv. In the Introduction to the Rintekno Report to Gassnova (Rintekno, 2010) it is stated that “Preferably the amine concentration shall be measureable online down to low levels (Limit Of Detection (LOD) < 0,1 ppmv) and shall form part of a comprehensive Continuous Emission Monitoring System (CEMS) for a Carbon Capture and Storage (CCS) plant.” It is noted that these values for emissions relate to the parent amines. It would seem that the emissions of any degradation products may well be less than the parent solvent (i.e. amines or alkanolamines). Thus any online techniques suitable for the determination of degradation products are likely to require greater sensitivity than required for the determination of the solvent emissions.

Recommendations as to the type of online (CEM) systems applicable to amine-based capture plants are obviously difficult as even the listing is dependent upon the practicality of such systems being installed to measure the relevant emissions from plants similar to that of the proposed Mongstad plant (CCM). No attempt has been made to list the systems according to price as this information is frequently commercial-in-confidence. Obviously, it would be a requirement of the suppliers to demonstrate the relevant sensitivities for the analytes of interest and freedom from appropriate interferences having regard to the overall composition of the exhaust gas. If an extractive sampling system was to be used (generally through heated lines), the integrity of the sample has to be demonstrated. The following commercially available systems are recommended:

- IR multicomponent analysers (including DOAS systems) – this may eliminate the need for an extractive system.
- Chemiluminescence technique comprising an ion chromatograph and possibly a Thermal Evolution Analyser (TEA). An extractive system is required and such a system needs to be verified.
- Total hydrocarbon analyser (FID) without a chromatograph or with a chromatograph if speciation of the hydrocarbons is required. Again an extractive system is required.

It would be possible for compounds that are amenable to GC analysis (suitable volatility, basicity and polarity) to combine the latter two techniques into a system, where the sampled gas stream into the TEA and the GC/FID. The above systems may be applicable to installation in an amine-based carbon capture plant. The above systems should be readily applicable to installation in an amine-based carbon capture plant. If non-commercial systems were to be used (and the brief for this report was to evaluate only commercially available systems), consideration should be given to use of mass spectrometry e.g. LCMS or GCMS (see Tibbett et al., 2010) in combination with some form of manual sampling (see Azzi et al.,

2010). Such systems could incorporate automated sampling direct to the instrument. This would require the investigation of purpose built equipment for the latter task.

The selection above is based on the need to measure the majority of the analytes identified as being present in the ducts of CCM type plant. Thus an IR system is appropriate. CSIRO's PCC pilot plants in Australia have been equipped with extractive FTIR systems to measure species such as CO_2 and NH_3. Such systems have performed well but it is unknown whether these systems have the required detection limits for the range of analytes (specifically, degradation products) possibly present.

Also, there are benefits if the online analysis system (or CEM) is “licensed" by appropriate international or national authorities (e.g. USEPA) for use in applications such as measuring the emissions in exhaust ducts i.e. they are demonstrably fit for purpose and therefore negotiations with government environmental bodies are readily facilitated. Multi-channel IR systems that do not use or rely on an extractive systems should be used if there is any concern that degradation of the extracted samples is possible; however if it is known that a certain product of this degradation or a derivatised product can be formed as a surrogate species for measurement of the analyte of interest then that would obviously be acceptable. Equally, if it is demonstrated that any degradation is minimal or cannot be detected in an extractive online sampling and analysis system then such a system is also obviously appropriate. It is likely that it will be possible to use online analysis to determine the amine solvents in the exhaust ducts of plants such as CCM but the effect of moisture especially the presence of any aqueous aerosols will require assessment. Although it is likely that the amines used in the solvents will be detected, the same cannot be unequivocally stated about the products of degradation as these are more than likely present at much lower levels in the exhaust duct but properties such as volatility and polarity (solubility) will be relevant.

Further research is required into the application of online analysis systems to determine the degradation products. In the absence of such research findings, that online systems can determine the analytes of interest at the concentration levels expected, then some assurance from the vendors is required.

It is thought that suitable on-line analysis systems (CEMs) for PCC plants will become available in response to changes to legislation. But at this stage, there is little incentive for manufacturers to develop techniques that may or may not be required in the future for such plants.

1 INTRODUCTION

This report is one of five that have been or will be completed to ensure that work in this project (Amine A) is finalised. The requirements for this study on online sampling and analysis are described as:

‘This part of the study will firstly list, describe and discuss pros/cons for the various online equipment/techniques which are available commercially at present, bearing in mind that these mainly are trace components. Next, a recommendation on which equipment/technique which will be best for each parameter (i.e. compound group), including the basis for this choice. Also, the probability for this choice of equipment/technique being successfully installed and operating at an amine-based CO_2 capture plant should be discussed.’

Online analysers will likely have a role in the optimisation and control of amine-based post combustion capture (PCC) plants and also in the estimation of atmospheric emissions from such plants. One of the limitations of online analysers is the relatively poor sensitivity achievable when compared with offline techniques comprising collection systems in which sophisticated and sensitive instruments can be used. Although, sampling may offer particular challenges in offline systems, if the analytes can be collected over an extended period of time without any loss or degradation occurring then the sensitivity is dependent upon the mass (volume) of gas collected.

As indicated in the reports of Project A Tasks 1 and 2, the materials used for the construction of probes and how these materials are prepared and passivated prior to operations are likely to be important at the Mongstad facility. It is recommended that either stainless steel, quartz or Teflon be used for all wetted surfaces. As has been discussed in Halliburton et al., (2010), not all materials used commercially may be suitable and materials such as Teflon or quartz liners or 900 grade stainless may be required.

In the report on Task 2 (Azzi et al., 2010) it is stated that “international stack sampling methods usually stipulate heating the sampling probes and liners to above 100 °C to eliminate condensation within the sample tube.” Obviously heating is required to prevent condensation when the dew point of the gas in the exhaust duct is greater than ambient temperature and this heating is a factor in any extractive online sampling and analysis technique. Thus, if a heated probe and lines are required then the analytes have to be thermally stable at the temperature used (i.e. above the dew point of the exhaust gas) and non-reactive to the probe and lines.

Indeed in an early report on continuous emissions monitoring (CEM) for coal-fired power stations, Sloss (1997) states “care must be taken to ensure that the most suitable system is chosen from the thousands commercially available”. Due diligence is obviously required and specific systems must be assessed against applicability as well as capital, maintenance and running costs. The task is made even more difficult in that many of the species of interest are not yet confirmed as being present in these emissions and any information on expected levels in the exhaust duct is limited.

In a conventional power plant, stack emissions of environmental concern (apart from CO_2) generally include particulate matter, SO_2, NO_x, as well as minor quantities of other materials. In a coal-fired power station, this is likely to include volatiles species of Hg, As, Se and organic compounds (VOCs). Emissions from an amine-based CO_2 capture plant will differ.

Many species will be removed by reaction with the amine solvent. Solid particulate matter (if present) will also be washed out of the gas stream. The emissions from an amine-based CO_2 capture plants are open to much discussion as to the amount and nature of these emissions. As suggested by Halliburton et al., (2010), the atmospheric emissions from utilities equipped with amine based PCC systems will be subject to scrutiny and government regulation. As well, the selection of appropriate online analysers and analysis systems are discussed.

This report should not be read in isolation from those prepared by Halliburton et al., (2010), Azzi et al., (2010) and Tibbett et al., (2010). Part of the challenge of this report is to identify the species that may be able to be measured by the online analysers and suggest techniques that may be applied to the online analysis for such species.

On-line analysers used in fossil-fuel fired power plants or in solid waste fired plants i.e. for solid particulate matter, SO_x (generally SO_2) and NO_x are of little interest. However it is apparent that the measurement of CO_2 itself will be important as the very *raison d'etre* for these plants is the removal of this gas (note that the three CSIRO pilot PCC plants in Australia use FTIR techniques to measure this latter compound and other compounds such as SO_x and NO_x in the gas stream). Also, the identification and quantification of amines or alkanolamines and their degradation products in any materials released by the plant are required.

The use of amine solvents to capture CO_2 is not new and the process is a commonly used technology in certain applications. The basic process was patented over 80 years ago (Bottoms, 1930 – cited by Rochelle, 2009). In this process, an aqueous amine solution is used to absorb CO_2 from the flue gas. The CO_2 is then released from the amine by mild heating, compressed and stored in a geological repository. Although amine-based scrubbing as a means of reducing emissions of CO_2 from combustion processes e.g. fossil-fuelled power stations (see Rochelle, 2009) has been extensively studied, there has been relatively little research effort on the emissions (and subsequent environmental impact) from the worldwide adoption of the technologies to capture CO_2 from the combustion of fossil fuels.

During a recent conference, Attalla and Azzi (2010) stated that "emissions monitoring of the parent amine and degradation products is a necessity for extended operation of the solvent". However at the same conference, it was claimed by Kamijo (2010) of Mitsubishi Heavy Industries Ltd (MHI) that at a test on September, 2009 of that organisation's pilot plant indicated that no amine was detected and that "degradated amine was <2 ppm as vapour". It should be stated that these MHI results were not obtained on a full-sized plant.

Shao and Stangeland, (2009) state that "it is well known that amines in some applications represent a health risk, but there is a lack of knowledge on health risks related to amines used for CO_2 capture". The authors further state that monoethanolamine (MEA), currently the most commonly used amine in CO_2 capture processes "will in itself have no adverse effect to the human health, animals, vegetation and water organisms" but that other amines such as 2-amino-2-methylpropanol (AMP), methyldiethanolamine (MDEA) and piperazine (PZ) “are ecotoxicological and have low biodegradability". It is also claimed that emissions of compounds such as ammonia can result in eutrophication and acidification (by ammonium salts) in the environment; of course amines emitted from CO_2 capture plant will degrade to other compounds and "most of them will not have negative environmental effects". Moreover nitrosamines are possible degradation products. The authors suggest that carbon capture and storage (CCS) demonstration projects "with amine based CO_2 capture can only receive public funding if they address research activities on environmental impact of amines" and that "no commercial CO_2 capture plants based on amines should be built before the knowledge gaps are filled".

In an ideal amine-based absorption system, the solvent is recycled and thus reused continuously. However, the commonly used MEA-based solvent has a relatively high vapour pressure and this may lead to significant solvent loss. Also, MEA has a propensity to degrade and is known to react with flue gas impurities such as SO_2, NO_2, and O_2 (Bello and Idem, 2005; Goff and Rochelle, 2004). The reaction with O_2 may be particularly important for natural gas combined cycles (NGCC), as the gas is combusted with a high rate of excess air. It is stated that the “technology also produces a certain level of emissions of amines and other chemicals to the atmosphere” (Svendsen, 2007).

The summary report of Knudsen et al., (2009) contains information on the potential for amines to degrade to produce potentially toxic compounds such as nitrosamines and amides. Compounds that may be of interest in the monitoring in a post combustion capture (PPC) plant using amines have been identified by the collaborators in the construction of the CCM plant and these are listed in Table 1.

Table 1. Compounds of possible interest in studies of the CCM plant

Class	Compound	Formula
Aldehydes	Formaldehyde	CH_2O
	Acetaldehyde	C_2H_5O
Alkylamines	Methylamine	CH_3NH_2
	Ethylamine	$CH_3CH_2NH_2$
	Dimethylamine	$(CH_3)_2NH$
	Diethylamine	$(CH_3CH_2)_2NH$
Amides	Formamide	$HCONH_2$
	Acetamide	CH_3CONH_2
Amines (and Alkanolamines)	Monoethanolamine (MEA)	$H_2NCH_2CH_2OH$
	Diethanolamine	$HN(CH_2CH_2OH)_2$
	Piperazine (PZ)	HNC_4H_8NH
	1,2-Diaminoethane	$H_2NCH_2CH_2NH_2$
	2 Amino-2-methyl-1-propoanol (AMP)	$(CH_3)_2C(NH_2)CH_2OH$
	N-Methyldiethanolamine (MDEA)	$CH_3N(C_2H_4OH)_2$
N- Nitrosamines	N-Nitrosodimethyamine (NDMA)	$(CH_3)_2N_2O$
	N-Nitrosodiethyamine (NDEA)	$(C_2H_6)_2N_2O$
	N-Nitrosomorpholine (MNOA)	$C_4H_8N_2O_2$
	N-Nitrosopiperidine (NPIP)	$C_5H_{10}N_2O$
	N-Nitrosodiethanolamine (NDELA)	$(CH_4OH)_2N_2O$
	N-Nitrosopiperazine	$C_4H_9N_3O$
	1-4-Dinitrosopiperazine	$C_4H_8N_4O_2$

To this list could be added, ammonia, NH_3, which is ubiquitous as a degradation product of amines. Process monitoring and emissions monitoring using online instruments are obviously desirable if not necessary in carbon capture plants. Online monitoring is common in fossil fuel powered utilities, but can be expensive (see for example, Sloss, 1997).

Listed on the world wide web are many sampling and instrument suppliers. These include:
Applied Analytics, Inc.: http://www.a-a-inc.com/cem_analyzer.htm
Analytical Systems International KECO: http://www.asiwebpage.com/index.php
B-R Controls Pty Ltd: http://www.brcontrols.com.au/index.php
ECOTECH AUSTRALIA: http://www.ecotech.com/

Enviro Technology Services Plc: http://www.et.co.uk/
Galvanic Applied Sciences Inc.: http://www.galvanic.com/
Jusun Instrument Co. Ltd http://www.jusun.com.tw/com_en.asp
Lear Siegler Australasia: http://www.lear-siegler.com.au/
LumaSense Technologies: http://www.lumasenseinc.com/EN/
Midac Corporation http://www.midac.com/
OPSIS AB (Swedish): http://www.opsis.se/
Particle Measuring Systems: http://www.pmeasuring.com/home
Thomson Group of Companies: http://www.thomsongroup.com/
Thompson Scientific: http://www.thermoscientific.com/wps/portal/ts/HOME

There are also websites in which instrument manufacturers are collated by type. See for example, Environmental Expert, http://www.environmental-expert.com/technology.aspx?word=Continuous%20Emission%20Monitoring%20(CEM)%20Systems

Many of those listed above are international companies but obviously the listing does have a bias in that all of websites listed in this report are in the English language. The listing is not complete but it does provide an indication of the diversity of approaches taken to emission monitoring. It is obvious that whatever emissions monitoring system is used, it is required that such a system is licensed by the relevant environmental body in a given country (i.e. government department or private association). Alternatively, either the manufacturer or the user must satisfy the authorities that the system is accurately measuring the relevant species and not some other species or artefact.

Other websites that contain information on instruments that may be suitable as detectors for CEM systems include:

- Advanced Chromatography Systems, USA Website: http://www.advancedlcgcs.com
- Cambridge Scientific Instruments, UK http://www.camsci.co.uk

In a recent report completed for Gassnova SF, (Rintekno, 2010), there is information from a number of suppliers of CEMs on the determination of amines in the exhaust ducts of amine-based carbon capture plants. Note that Rinteko Oy was acquired by Neste Jacobs in 2008, www.rintekno.com/ but the company trades under the name of Rintekno Oy.

- The companies surveyed in this report by Rintekno to Gassnova SF include:
- Agilent Technologies, USA http://www.home.agilent.com/agilent/home.jspx
- Baseline Mocon Inc, USA http://www.baseline-mocon.com/
- California Analytical Instruments, USA http://www.gasanalyzers.com/
- Cascade Technologies, United Kingdom http://www.cascade-technologies.com/
- CEM Specialties Inc., Canada http://www.cemsi.on.ca/
- Cerex Monitoring Solutions LLC http://www.cerexms.com/
- Cromatotech, France - no website found
- EcoChem Analytics, USA http://www.ecochem.biz/
- Environics Oy, Finland http://www.environics.fi/
- FluxSense AB, Sweden http://www.fluxsense.se/
- MIDAC Corporation, USA http://www.midac.com/
- Sick Maihak, Germany/Sweden http://www.sick.com/group/EN/home/Pages/homepage1.aspx
- Siemens http://www.siemens.com/entry/cc/en/

In summarizing the findings gained from the companies, the following three different techniques for the measurement of amine emissions were reported as encouraging:

- Infrared (IR) Spectroscopy (mainly FTIR);
- Gas Chromatography
- Ion Mobility Spectroscopy (IMS)

Rintekno (2010) report that all vendors "suggested using a heated sampling system but there were no exact proposals to how such an amine sampling system would be designed. All the suggested techniques have a LOD of < 0,1ppmv for MEA. The FTIR technology seems to be the most promising one for measuring amines in the treated gas at the top of the absorption tower."

OPSIS AB based in Sweden (http://www.opsis.se/) was not one of the companies surveyed. This company can supply Differential Optical Absorption Spectroscopy (DOAS) for online analysis or for use in CEM systems; these seem to be applicable in amine-based carbon capture plants (see the section, Conclusions and Recommendations).

It must be stated that the vendors were only asked to respond on the requirement to measure amines in the exhaust and not both the amines and their possible degradation products, which, if present are likely to be at even lower levels than the amines from the solvents. The volatility and polarity of each degradation product are factors in their occurrence in the exhaust. Thus Henry's Law Constants (for example, see http://www.henrys-law.org i.e. Sander, 1999) are applicable when any attempt is made to determine the distribution/partitioning of the amine solvent and the degradation products between the aqueous, the aqueous aerosol and the purely gas phases produced within the exhaust duct after washing. Of particular importance, when determining the emissions from amine-based plants is the distribution of species between the aerosol (and the amount of this phase emitted) and the gas phases.

Relevant to the measurement of emissions from plants such as CCM are many of the offline standard procedures written by or for the USEPA, e.g. the USEPA describes 101 methods in the database for the 1-99 series applicable to stationary sources and also 17 methods in its TO (Toxic Organics) series, applicable to monitoring ambient air i.e. USEPA TO1 to USEPA TO17 (see references for examples). There are also commercial laboratories, that offer services based on USEPA methods (or similar) for air testing (e.g. Columbia Analytical Services, Inc. http://www.caslab.com/). Promulgated methods of the USEPA can be found at the website of Technology Transfer Network, Emission Measurement Center of the EPA. http://www.epa.gov/ttn/emc/promgate.html .

Applicable sampling methods are discussed in the report by Azzi et al., (2010) and the analytical methods are discussed in the report by Tibbett et al., (2010); see also a summary of applicable methods in the Appendix for the various analytes listed in Table 1.

Table 2. Typical Composition in Gas in Exhaust Duct

Treated Flue Gas	Typical Values
Flow (kg/s)	400
Temperature (^oC)	25-50
Pressure	ambient
O (mol %)	15
N (mol %)	81.5
CO_2 (mol %)	0.5
NO_x (ppmv)	?
NO_2 (ppmv)	?
NH_3 (ppmv)	<50
SO_2 (ppmv)	?
H_2O (mol %)	3
Amines (ppmv)	<5

Obviously any commercial system must be able to representatively view or sample the typical exhaust duct of an amine based carbon-capture plant as described below in Table 3.

The selection of suitable commercially available online analysis techniques is challenging not only for use in the exhaust duct of CCM but generally. The analytes, listed in Table 1 as well as ammonia and some of the solvent amines may or may not be present in the exhaust duct of the amine based carbon capture plant to be built at Monstad but they are possible degradation products from such as plant utilising amine-based solvents. The sampling regime has been discussed in the reports of Project A, Tasks 1 and 2 (Halliburton et al., 2010 and Azzi et al. 2010) and the analytical techniques that could be applied to a range of samples taken from the plant (not only the exhaust gas) are detailed in the report of Task 4 (Tibbett et al., 2010). The findings in these reports are generally applicable in the discussions in this report. Of particular interest in this section is the report of Task 4. Whether the species (listed in Table 1.) are present in concentrations amendable to measurement by online techniques and CEMs is still a matter of continuing debate (and this is frequently of a commercial nature).

The reactive nature of many of these gases from PCC plants, their possible presence in both gaseous and particulate forms (i.e. in aerosols), and their low concentration in the duct are all properties that make their determination difficult. Typical duct properties are given in Table 3.

Table 3. Typical Dimensions and Conditions of CCM

	Full Scale Plant	Pilot Plant
Gas flow Sm^3/h	0.72 – 2.3 Million	250 - 1200
Pipe Construction	Stainless Steel or Plastic	Normally Stainless Steel
Absorber cross section	Rectangular or circular	Normally circular
Gas Conditions	Saturated, atmospheric pressure + dynamic delta P	Saturated, atmospheric pressure + dynamic delta P
Gas Temperature (^oC)	25-50	25-50
Gas velocity at exit (m/s)	Approximately 20	

2 ONLINE ANALYSERS

2.1 General

The main purpose of online analysis of a stream in a process plant (in this case the emissions from an amine-based carbon capture plant) is to provide real-time, continuous monitoring of key components for process and emissions assessment and to enable an operator to respond to a change in the process. The emission stream from an amine-based capture plant such as CCM flue may consist of gas, liquid or solid (although the presence of solid particulate matter is unlikely) or a mixture of any two or all phases at certain ranges of temperature, pressure and flow rate.

Generally, it is wise to position the sampling point for online analysers such that any gas stream containing fine solids and liquid aerosols are sampled isokinetically (i.e. the velocity of the sample stream into the nozzle of the collection device is equal to the velocity of the bulk gas flow). As stated by Halliburton et al., (2010) "When aerosols are present in the exhaust gas it is most likely that isokinetic sampling will be required" and "it is assumed that at the proposed Mongstad plant, the Stokes diameter of the aerosol droplets in the flue gas will be sufficiently large to require isokinetic sampling". Also, many of the analytes of interest are polar and are thus soluble in water and maybe dissolved in the liquid droplets. Representative sampling of both the gas and liquid (aerosol) phases is required, as some species will be partitioned between these phases.

There are challenges in placing online analysers (or CEMs) in the exhaust ducts of plants; these include the positioning in an industrial location, corrosive species, exhaust gas temperatures, dew points and indeed temperature variations (for example, see Johnston and Baum, 2005). CEMs also include the often more analytically sensitive combinations of samplers and analysers, although these systems are designed to work in a discontinuous manner

Ideally, the online monitoring (CEM system) should have the following characteristics to enable precise and effective process monitoring:

- It should be sensitive and selective to the range of variation in the concentrations in the properties (or compounds) of interest.
- Its performance should not be affected by the variation in other bulk properties of the stream or should have an inbuilt mechanism to compensate any such interfering variations so as to give accurate measurement under all conditions.
- It should not be physically or chemically attacked by the steam within the duct.
- Its rate of response should be faster than the rate of change of property it measures.
- It should not be affected by surrounding electric, electronic, mechanical, thermal, magnetic or radiation devices or conduits carrying input to or output from these devices, or the probe should have inbuilt mechanism for operating in environment with any or all of these surroundings
- The system should be able to continuously perform without significant maintenance at least for a year to allow for checking, refurbishment or replacement during the scheduled annual maintenance of the plant
- The system should have an output that is compatible with a variety of data processors.

The design of the sampling system is reliant on knowledge of the physical and chemical characteristics of the analytes (see Halliburton et al, 2010; McGowan, 2005). The nature of sampling systems and materials of construction are discussed more fully in the reports of Task 1 (Halliburton et al., 2010) and Task 2 (Azzi et al., 2010).

The United States Environmental Protection Agency (USEPA, 1997, http://www.epa.gov/ORD/NRMRL/pubs/625r97001/625r97001.pdf) describes the two important processes when monitoring emissions from stationary sources:

- Extraction of a representative sample
- Analysis of that sample for the analytes of interest

Both extractive techniques and in-situ methods are used to monitor concentrations of analytes directly in the exhaust ducts of stationary plant such as the CCM. In extractive techniques, vapour and aerosols are withdrawn from the stack, conditioned and then analysed. Whereas, in in-situ systems, the vapour and aerosols are not extracted, but are analysed directly in the duct. There is a third mode of operation i.e. “indirect parameter monitoring” where plant operational or control equipment parameters are correlated to emissions that are determined by manual or instrument reference methods (USEPA, 1997) This third mode of operation is not discussed in this report as in the indirect parameter monitoring, parameters are correlated to emissions determined by manual or instrument reference methods and although it may be a suitable approach, it is not a requirement for this report.

Continuous emission monitoring is also discussed on the USEPA Technology Transfer Network, Emission Measurement Center website, http://www.epa.gov/ttn/emc/monitor.html

The handbook of CEMs for Non-Criteria Pollutants (7 chapters plus an appendix) can be downloaded from the USEPA Technology Transfer Network, Emission Measurement Center, Continuous Emission Monitoring - Information, Guidance, etc. website, http://www.epa.gov/ttn/emc/cem.html

The Advanced Monitoring Systems Center of the USEPA has verified technologies that are or may be applicable to the measurement of analytes in the exhaust duct of an amine-based carbon plant http://www.epa.gov/etv/vt-ams.html e.g. listed are seven companies that produce (or market) NH_3 detectors that have been verified for use in animal husbandry. There are also two listed companies (OPSIS AB and Siemens Laser Analytics AB) that produce systems for use as CEMs for the determination of NH_3.

2.2 Chemiluminescence

This technique is generally applied to the determination of NO_x but may also be used for the determination of NH_3. The technique is based on the reaction of NO with O_3 to produce excited NO_2 molecules that fluoresce when the excited molecules return to their ground state. Thus, the technique is applicable to nitrogen-containing compounds that can generate NO.

In an early review, Isacsson and Wettermark, (1974) report that NH_3 could be converted to NO and that a chemiluminescence detector could be used to measure NH_3 by changing the conditions of catalysis.

Based on chemiluminescence is the Thermal Energy Analyser (TEA) which has very good sensitivity and selectivity for nitrogen containing compounds and it is possible that it may be applied to the monitoring of emissions of these compounds. It is interfaced with a gas chromatograph (GC/TEA); this provides chromatographic separation of the nitrogenous compounds, and thus provides selectivity to these compounds. Current systems are available with three modes of operation for the determination of nitrogen, nitro and nitroso-compounds. The GC/TEA would only be suitable for compounds amenable to gas chromatography systems, such as volatile nitrosamines and possibly some amines, although these compounds as well as the amides perform relatively poorly on GC systems due to their basicity and polarity. Certain of the higher alkanolamines would also be problematic due also to their low volatility, as discussed in detail by Tibbett et al (2010).

There are two related companies, which supply these instruments i.e. Advanced Chromatography Systems, USA, http://www.advancedlcgcs.com and Cambridge Scientific Instruments, UK, http://www.camsci.co.uk . This latter company can also provide services in Germany through its partnership with Unicam. These companies supply chemiluminescence instruments that may be used as detectors for chromatographs. These could be used in CEM systems, if a suitable extractive sampling system was devised i.e. the sample of gas could be taken via a loop and injected directly in a GC. Altenatively a cold trap could be used; this would have to cyclically heated to release the analytes into the GC. If moisture was a problem some form of drying may be required but care has to be taken with polar compounds. This is a non-trivial exercise but it may be worthwhile.

It should be noted that as the chemiluminescence from the reaction of NO with O_3 occurs in the UV region, the technique is somewhat associated with sub-section 2.3 4 (UV detectors). It is unique in its mode of operation and because of its possible role in CEMs, it has been addressed separately in its own sub-section.

2.3 Infrared Systems

Infrared systems compare absorption of the sample gas against a reference (calibration) gas or gases. Sampling could be either an extractive technique or in-situ (as described previously). The latter has some advantages in that farther degradation of the amines and other compound cannot occur in the “inert” lines used to obtain an extracted sample. However, it is noted that generally the company respondents to the survey by Rintekno on the application of CEMs to the measurement of amines (Rintekno, 2010) support the use of IR spectroscopy with extraction using heated lines.

Baker et al., (2004) state the advantages of infrared gas analysers used at waste-to-energy facilities. The authors quote impressive figures in Table 3 of their paper for the relative accuracy of third-generation hot-wet multicomponent IR analyser-based CEMS for species such as CO, NO_x and SO_2 at ppm levels. Whether the detectability and accuracy can be achieved for other species in the exhaust ducts of amine-based carbon capture plants is unknown. Barber et al., (2005) give extensive details of IR spectroscopy and spectrometers.

Infrared systems include variants of the technique such as:

- gas filter correlation infrared (GFCIR) – the advantage is that the system can tolerate interferences and can monitor several gaseous species simultaneously
- non-dispersive infrared (NDIR) – the IR source is modulated and are used for the single measurement of certain species e.g. CO, CO_2 or SO_2 in coal-fired power stations (Sloss, 1997); the systems are commonly used in extractive CEM systems, although they can be used in-situ.

- Fourier transfer infrared (FTIR) – this technique is low maintenance and is used in both extractive and in-situ systems – the systems are also capable of measuring different analytes simultaneously.

A schematic diagram from the USEPA Test Method 320, Measurement of Vapor Phase Organic And Inorganic Emissions by Extractive Fourier Transform Infrared Spectroscopy (FTIR) is given in Figure 1. Refer to http://www.epa.gov/ttn/emc/methods/method320.html

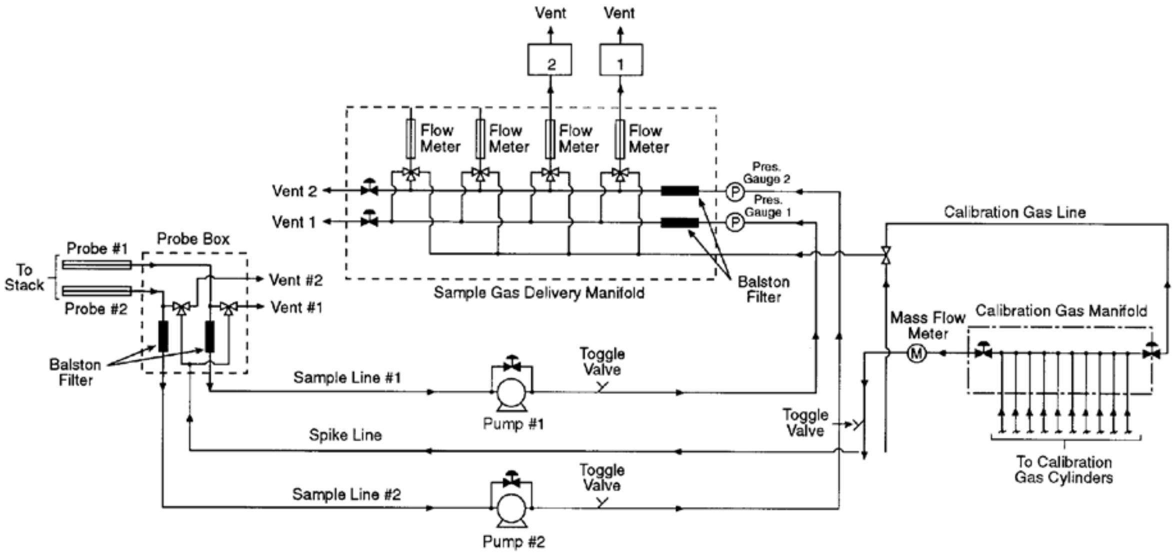

Figure 1. Extractive FTIR sampling system (copyright USEPA),

There are also versions that make use of lasers; one of these is the subject of a verification report to the USEPA by Battelle (Meyers et al., 2000). Figure 2 is taken from that report.

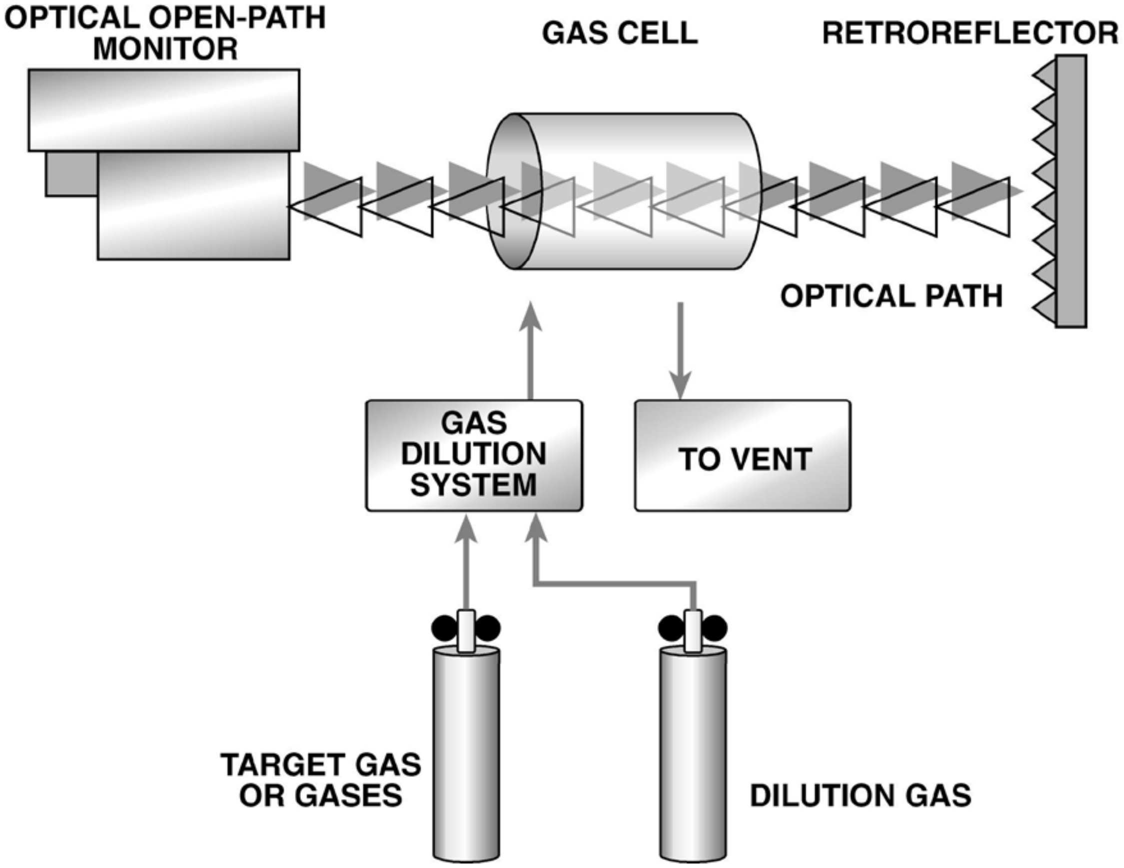

Figure 2. UNISEARCH Associates LasIR TDL Open-Path MonitorSystem (copyright USEPA, 2000).

2.4 Ultraviolet Systems

Ultraviolet (UV) systems are based on the absorption of ultraviolet light at specific wavelengths by gaseous analytes. In a carbon capture plant, the species of greatest interest would be amines and NH_3 (and probably N-nitrosamines). Again, an in-situ technique for sampling would be the most desirable although the formation of degradation products requires study.

There are three basic systems available

- Non-dispersive ultraviolet (NDUV)
- Second derivative of absorption spectra (SDAS) in which the UV beam is passed through the sample and the detector measures the signal at a set wavelength or wavelengths if more than one species is being measured.
- Differential optical absorption spectroscopy (DOAS) systems in which the spectrum used is in the UV range (see section, 2.5).

Johnston and Baum, (2005) in their book chapter write in some detail on the measurement methods used in the UV and on the application of UV systems in continuous emission monitors.

2.5 DOAS Systems

DOAS is a method used to determine concentrations of gases at trace levels (although the limit of detection has not been demonstrated for the analytes of interest in the emissions from CCM). Generally, the narrow band absorptions specific to the analytes' structures in the UV and visible spectral region are measured although the IR region can also be used and this may have greater applicability in the CCM plant. A typical DOAS instrument consists of a continuous light source, e.g. a Xenon-arc lamp or IR source and an optical setup to send and receive the light through a set light path; this can range from several metres to many kilometres. A schematic of a UV-visible system is given in Figure 3. An Infrared DOAS system is illustrated in Figure 4.

In a carbon capture plant, the path length used would be the width of the exhaust duct (i.e single pass), although a number of light passes across the duct could be used to increase the sensitivity of the system.

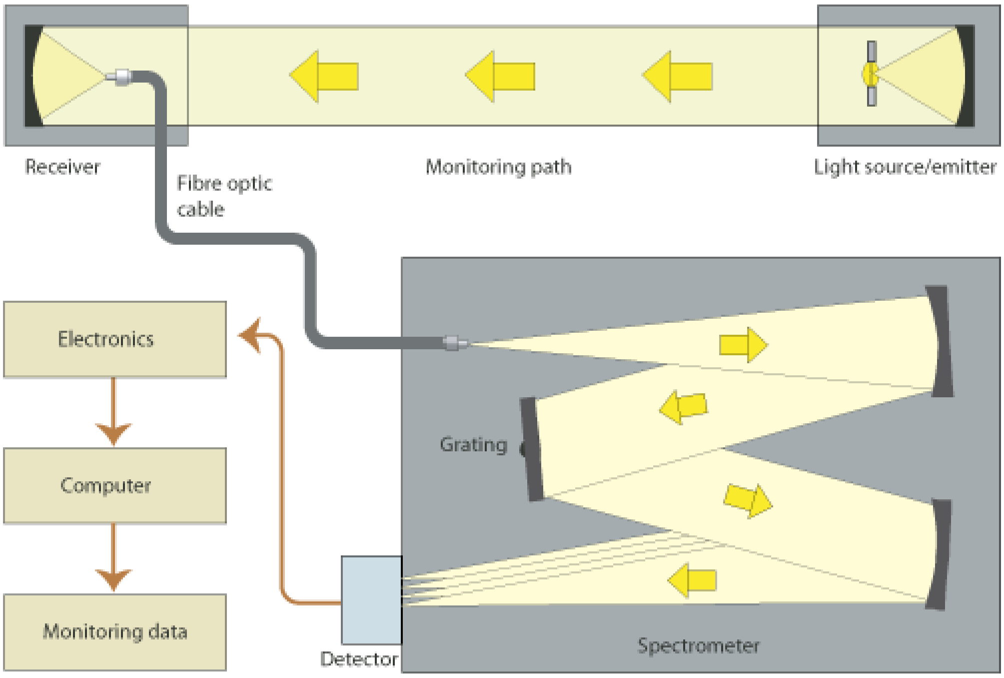

Figure 3. General Schematic of a DOAS System (copyright, OPSIS - http://www.opsis.se/)

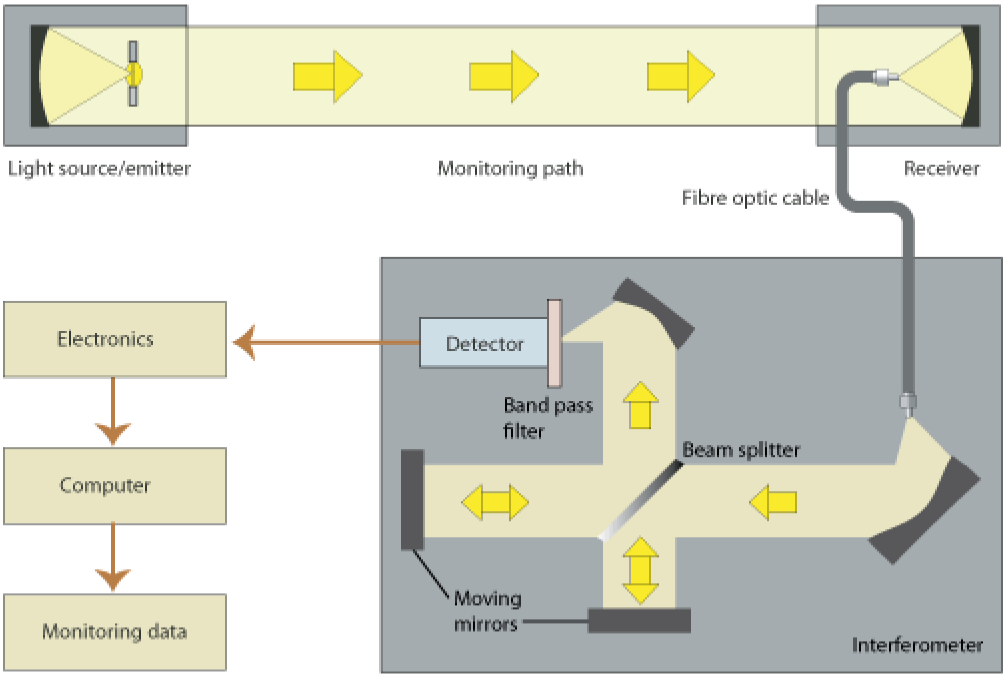

Figure 4. IR DOAS System (copyright, OPSIS - http://www.opsis.se/)

2.6 Flame Ionisation

Flame ionisation detection (FID) can be used for the determination of total hydrocarbons or may be used in combination with gas chromatography which is used to separate the hydrocarbons (see below). Note that the sensitivity of the FID to compounds may be significantly reduced for compounds containing N. O, S or Cl i.e. in those compounds where there are reduced hydrocarbon moieties. Response factors are linear for hydrocarbons but have to be ascertained for each non-hydrocarbon compound present.

2.7 Gas Chromatography

Gas chromatography (GC) equipped with FID can be used in extractive online systems (e.g. a loop system). It is not truly continuous as the analysis time can be significant (indeed any extractive system cannot really be called continuous as there is always some delay in transferring the sample from the duct to the analyser).

2.8 Mass Spectrometry

There is a number of techniques that may be applicable although each of these may not be suitable for installation near the exhaust of a carbon capture plant.

The techniques include:

- Gas chromatography mass spectrometry (GC/MS).
- Gas chromatography, tandem mass spectrometry (GC/MS/MS).

- Liquid chromatography mass spectrometry (LCMS).
- Proton-transfer reaction mass spectrometry (PTR-MS).

Most of the above are commonly used in organic analytical laboratories world-wide for offline determinations of trace level compounds in may applications Of more specific application is the PTR-MS instrument, available from Ionicon Analytik (founded in 1998 as a spin-off company of the University of Innsbruck, Austria) http://www.ptrms.com/ . The technique is generally used for the detection of gaseous organic compounds (VOCs) in the atmosphere (both natural and anthropogenic). The technique has recently been reviewed (Blake et al., 2009). The main limitation of the technique is the requirement that only known compounds can be monitored and it must be determined that no other compounds are present at the target mass monitored. This can become difficult at higher masses in complex matrices, where other components may be present at the same mass as the target compound. Hence a thorough understanding of the characteristics of the matrix and the components present is required. The main advantage is that it can be used in real-time to monitor changes in concentration of known compounds. The main use of this technology is the measurement of emissions (VOCs) or concentrations of such in the Earth's atmosphere. They are not as yet supplied commercially as online analysers in the industrial sense. It is stated by Blake et al. that "The high sensitivity of the system which has now been reached allows for continuous emission control and monitoring of VOCs in urban and also clean rural environments." Lindinger et al., (1998) describe a system using PTR-MS in an online analysis system for the determination of VOCs but there does not appear to be a system commercially available.

Veltman et al., (2010) used mass spectrometric techniques to monitor the environmental and health impacts of amine solvent emissions from PCC plants (although these were not online techniques). Wada, and Sterling (2001) in their paper discuss the development of a mass spectrometer-based continuous emission monitor for volatile organic compound emissions from combustion devices. But the sophistication of MS-based systems and the need for care in their implementation may work against such systems.

2.9 Ion Mobility Spectroscopy (IMS)

On the Jusun Instrument Co. Ltd website the use of Ion Mobility Spectroscopy as a CEM system is discussed i.e. the use of the technique in the monitoring of NH_3 is described, It has been used to determine the concentration of NH_3 in the exhaust duct of a power station in the US in which the level of NH_3 can be used for control of systems to accommodate fluctuating levels of NO_x and to monitor the characteristics of catalysts in selective catalytic reductor (SCR) units. It was claimed that good precision and accuracy were obtained in this situation although no data are available (commercial-in-confidence). See Bacon, (2002) at http://www.jusun.com.tw/IMS%20Application%20for%20CEM.pdf . In an earlier paper, Bacon et al., (1991) state that IMS would be suitable for use as an on-line analysis technique. This technique is apparently not even now widely used for this purpose (almost 20 years later).

The theory of the IMS technique is described in the following website: http://www.pmeasuring.com/wrap/filesApp/app54_IonMobility/file_1/molecular_app54IMS.pdf

IMS is an ionization-based time-of-flight technique. The technique is illustrated in Figure 5. A continuous ambient air sample is drawn over a semi-permeable membrane, through which the analyte molecules permeate and are transported by dry air to the reaction region. The transported analyte is ionised by low-level beta energy (from a nickel-63 source). Under the influence of an electrostatic field, the ionised analyte is separated by a shutter from interferents and the ions produced are counted at a Faraday plate. The current produced is amplified to produce a time-of-flight spectrum. This evaluated for the specific analyte and the concentration based on the peak height (current) is determined.

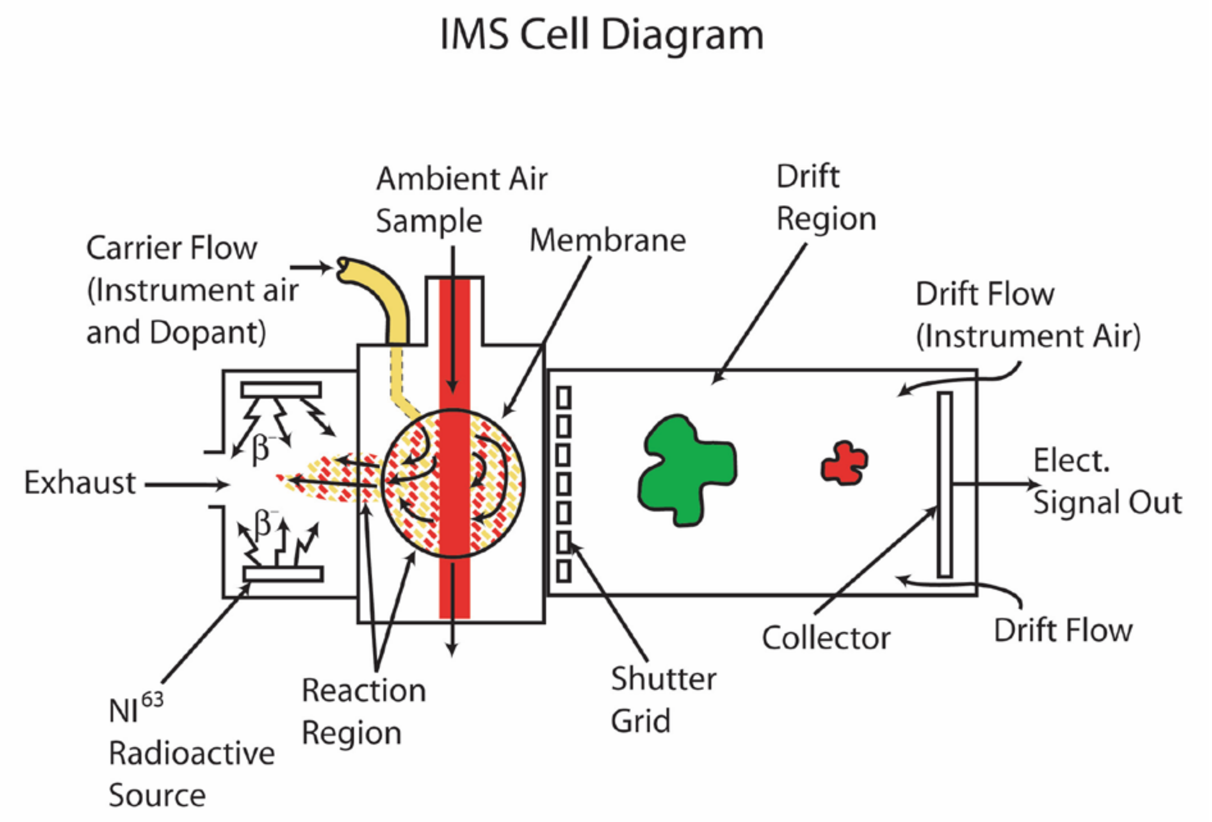

Figure 5. Schematic diagram of detector for Ion Mobility Spectrometer (copyright, A2C2 Magazine).

This technique may be suitable for the detection of specific compounds at CCM but to-date it does not appear to have been considered widely for application in related plants.

2.10 Photoacoustic Spectroscopy (PAS)

A schematic diagram of the system used in the Innova 1314 and 1412 instruments is shown in Figure 6.

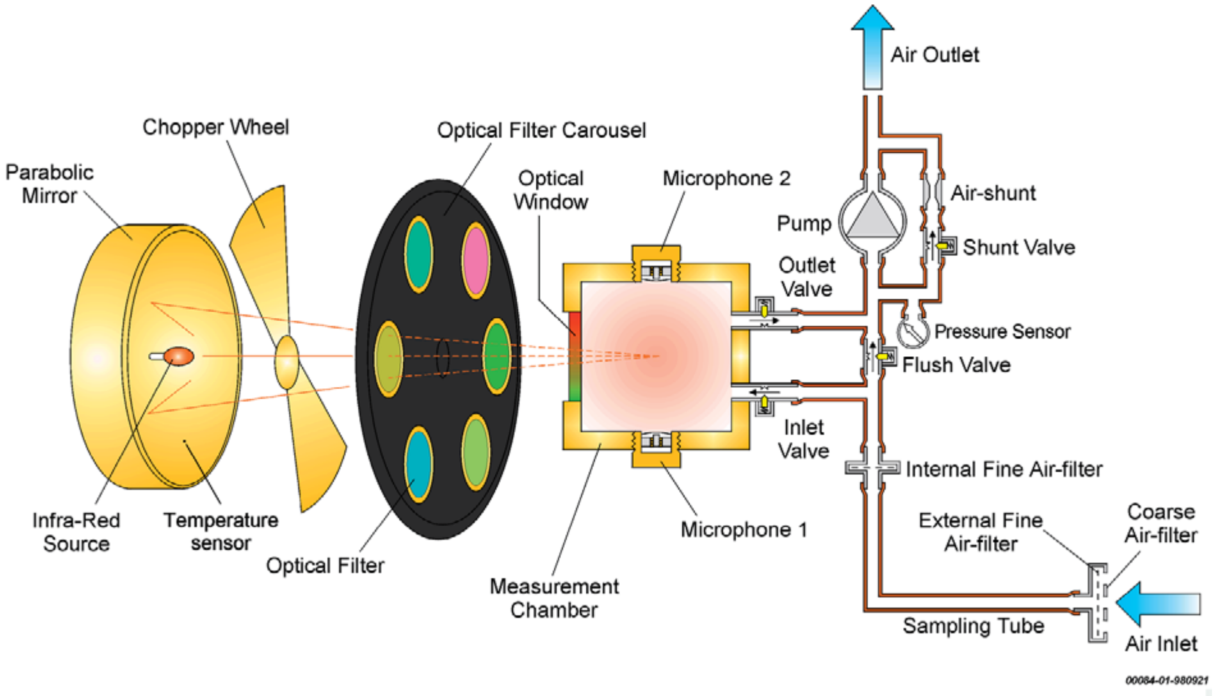

Figure 6. Diagram of photoacoustic system (PAS) used in the Innova Instruments (copyright, LumaSense Technologies).

Pogány et al., (2009) discuss the use of near-infrared photoacoustic spectroscopy in conjunction with pre-concentration collection of NH_3 gas onto WO_2. The technology is not commercially available as a CEM system and a means of handling any entrained water vapour has to be accommodated before such as system is feasible for the CCM plant.

2.11 Further Research

Evans et al., (2006) for the (US) Electric Power Research Institute EPRI on the potential use of “miniature, micro and nano technologies” for miniaturising gas sensors in the power industry (what is applicable in this industry is probably applicable to PCC plants). One of the the points made by the authors that the development of CEM systems is driven by regulation (this may be a factor in the future for PCC plants but it is not currently the case) and that most of the miniature sensors are designed to monitor gases in the ambient atmosphere. It would seem that without demand driven by regulation, there may be little research done in this area. This may be the case for research generally into online analysers for CCM type plants.

However, if sensitivity remains an issue for online analysis, then further experimentation will be required. If there is a requirement to assess the potential for the emissions to be damaging in the atmosphere, it is suggested that one approach to this experimentation will require the use of the smog chamber, similar to that located at the CSIRO laboratory at Lucas Heights. There may also be a way to sample the exhaust into a “mini smog” chamber equipped with UV lights and suitable analysis equipment, FTIR and MS techniques (possibly PTR-MS).

Indeed some work on the formation of degradation products from MEA has been reported by Nielsen et al., 2010. This team used sophisticated techniques including mass spectrometry.

3 PROS AND CONS OF COMMERCIALLY AVAILABLE ONLINE TECHNIQUES

The details of the various techniques are reported in Section 2. However, it should be remembered that to even validate reference methods for non-criteria pollutants (as specified by the USEPA) such as amines and their degradation products is difficult. There are challenges for both wet chemical reference methods and instrumental monitoring techniques.

Tibbett at al., (2010) has reported on the various methods that are applied to the determination of many of the compounds listed in Table 1 (above). Many of these methods are available from the websites of the Occupational Safety and Health Administration of the US Dept of Labour http://www.osha.gov/ , of the United States Environmental Protection Agency and of the United States National Institute for Occupational Safety and Health.

3.1 Is drying possible?

If the sample is to be collected in a dry form prior to analysis then some form of dryer such as Nafion tubing may have to be used. The website of the company Purma Pure provides information of the retention various compounds if this material is used. According to Purma Pure, the following are retained (i.e. not lost to the aqueous phase): aldehydes (i.e. generally non-polar compounds); the species of interest that are likely to be lost to some degree (if not totally) are: amides, amines and ammonia (i.e. polar compounds). Thus, as most of the species of interest identified as likely to be present in the exhaust are polar compounds, it is reasonable to conclude that drying of the sampled gas is not desirable. See http://www.permapure.com/support/tools-calculators/?ind=customer-applications .

Thus is likely that some form of heating will be required and if heating is used than it may be reasonable to use some form of extractive technique although the stability of the analytes under the conditions of extraction will need to be assessed.

3.2 Chemiluminescence

a) Pros: This technique is obviously of use for the determination of nitrogen containing compounds. With current systems it is possible to determine nitrogen, nitro and nitroso-compounds.

b) Cons: Any GC/TEA used as an online system would not be suitable for all compounds e.g. non-volatile nitrosamines and some amines due to their basicity and polarity. Also, higher molecular weight may be difficult because of their low volatility. Compounds that do not contain N (e.g. the aldehydes) would not be detectable.

c) It is doubtful that there is a system based on chemilumenescence could be installed successfully at a CCM-type plant

3.3 Infrared Systems

a) Pros: Infrared systems would be applicable to the determination of most of the analytes of interest in a CCM-type plant. FTIR systems have been used in the three CSIRO pilot plants in Australia.

b) Cons: Whether it is possible to individually measure all the analytes within the matrix of emissions from an amine-based CCM plant is still not known nor is it known whether the sensitivity required can be achieved by a commercial system. The FTIR systems in Australia use an heated extractive technique and have never been tested for their capability to measure the trace analytes listed in Table 1.

c) It is obvious that a FTIR system could be installed in the CCM plant but discussions are required with suppliers to obtain guarantees that the analytes can be measured at the concentrations required. At this stage, it is doubtful that the full range of specified analytes (see Table 1) could be determined at the levels likely to be present in the exhaust duct.

3.4 Ultraviolet Systems

a) Pros: Theoretically, the number of wavelengths available makes UV systems appealing but....

b) Cons: Ultraviolet (UV) systems are unlikely to be applicable as much of the UV spectrum is absorbed in air. Also the broad peaks observed in the UV suggest that interferences may pose problems.

c) It is unlikely that an UV system could be successfully installed as an online analyser in CCM-type plant.

3.5 DOAS Systems

a) Pros: DOAS is a method that measures the species of interest using a spectrometric approach in-situ. Such a technique using the IR spectrum would suitable for a CCM-type plant. The in-situ approach offers advantages over an extractive one in which the stability of the analytes has not been confirmed.

b) Cons: Whether the technique can offer the required sensitivity for the degradation products listed in Table 1. is unknown.

c) As mentioned in sub-section 3.3 (above), a DOAS system using the IR spectra could be installed in the CCM plant but discussions are required with suppliers to obtain guarantees that the analytes can be measured at the concentrations required.

3.6 Gas Chromotagraphy/Flame Ionisation

a) Pros: GC/FID is often the technique of choice for the determination of volatile organic compounds.

b) Cons: Some of the species listed in Table 1 are not volatile and GC/FID is not an appropriate technique. An extractive technique would be required and some derivatisation of the compounds may also be required prior to measurement. The technique is unlikely to be applicable without significant study and alteration. Sample handling is also an issue.

c) GC/FID is unlikely to be readily installed in a CCM-type plant without significant modification to any sampling system required.

3.7 Mass Spectrometry

a) Pros: In combination with GC, the techniques have wide application in determining many of the volatile analytes listed in Table 1.

b) Cons: The technique is sophisticated and is unlikely to be used in online analysis systems. It is the sophistication of the techniques and the need for stability and a clean environment that prevent its easy installation in operating plants. As mentioned in sub-section 3.7, sample handling is also an issue.

c) GC/MS or GC/MS/MS is unlikely to be readily installed in a CCM-type plant.

3.8 Ion Mobility Spectroscopy (IMS)

a) Pros: IMS have wide application in determining many of the volatile analytes listed in Table 1.

b) Cons: The interferences present in a mixed matrix likely to be present in the duct of a CCM-type plant have yet to be determined. An extractive technique is likely to be required. Moisture may be an issue.

c) IMS is unlikely to be readily installed in a CCM-type plant. This technique may be suitable for the detection of specific compounds but it does not appear to have been considered for such an application. Although in the Rintekno Report, IMS is mentioned as one of the techniques that may be applicable for the determination of amines in the emissions of solvent.

3.9 Photoacoustic Spectroscopy (PAS)

a) Pros: The technique does have wide application.

b) Cons: The technique is unlikely to be used in a duct of a CCM-type plant and it is not known whether it can differentiate the analytes and measure them at the concentrations likely to be required. Sample handling is also likely to be an issue

c) PAS is unlikely to be readily installed in a CCM-type plant, as it is does not seem to have the required sensitivity nor selectivity. Although approaches to manufacturers and subsequent discussions are required.

3.10 The Best System

Determining the “best” system for pn-line analysis is undoubtedly difficult as no generic “best system” exists (United States Environmental Protection Agency, 1997). Online systems depend upon factors such as regulatory requirements, analytes (pollutants), duct and ambient conditions, as well as cost but “low cost should never be the single deciding factor” (USEPA, 1997). Obviously the best system will be the one that can determine the analyte(s) at the required concentration(s) in a representative sample either extracted from the duct or in-situ. Low capital and maintenance costs are a bonus.

4 CONCLUSIONS AND RECOMMENDATIONS

Recommendations as to the type of CEM systems applicable to amine-based capture plants are obviously difficult. Some attempt has been made to list the systems on the basis of applicability below. The listing is dependent upon the practicality of such systems being installed to measure the relevant emissions from plants similar to that proposed to be built at Mongstad. No attempt has been made to list these according to price as this information is often commercial-in-confidence. Recommendations of commercially available systems are:

- IR multicomponent analysers (including DOAS systems) – it would be a requirement of the suppliers to demonstrate the relevant sensitivities for the species of interest and freedom from interference having regard to the overall composition of the exhaust gas. If an extractive sampling system was to be used (generally an heated line), the integrity of the sample has to be demonstrated.
- Chemiluminescence technique comprising a chromatograph and possibly a TEA. This would require the development of an extractive sampling technique.
- Total hydrocarbon analyser (FID) without a chromatograph or with a chromatograph if speciation of the hydrocarbons is required. An extractive technique would again be required.

It would be possible to combine the latter two techniques (depending on the selection of a suitable chromatographic column) into a system where the gas stream from the chromatograph was split into the TEA and the FID detectors. The above systems should be readily applicable to installation in an amine-based carbon capture plant if an extractive technique was seen to be suitable.

The selection above is based on the need to measure as many of the analytes as possible. Thus a multi-channelled IR system is appropriate. CSIRO’s PCC pilot plants in Australia have been equipped with extractive FTIR systems to measure species such as CO_2 and NH_3/ Such systems have performed well but it is unknown whether such systems have the required detection limits for the range of analytes in Table 1.

Obviously, there are benefits if the CEM or online analysis systems are “licensed" by appropriate international or national authorities (e.g. USEPA) for use in applications such as measuring the emissions in exhaust ducts (i.e. fit for purpose) as negotiations with government environmental bodies are readily facilitated. Multi-channel IR systems that do not use or rely on an extractive system should be used if there is any concern that degradation of the extracted samples would be a concern; but if it is known that a certain product of this degradation or a derivatised product can be formed as a surrogate species for measurement of the analyte of interest then that would obviously be acceptable. Equally, if it is demonstrated that any degradation is minimal or cannot be detected in an extractive online sampling and analysis system then such a system is obviously acceptable. It is likely that it will be possible to use online analysis to determine the amine solvents in the exhaust ducts of plants such as CCM but the effect of moisture especially the presence of any aqueous aerosols will require assessment. Although it is likely that the amines used in the solvents will be detected, the same cannot be unequivocally stated about the products of degradation. There are significant unknowns including their identity and the actual concentrations of these products in the duct and these may not be detectable by commercially available systems. Again the reactions of the polar degradation products with water droplets (including fine aerosol particles) are a factor that requires consideration.

The total “nitrogen loading” in the duct could be determined by an online technique using Chemiluminescence (including TEA); a technique using a FID could be used to estimate the emissions of organic compounds. Chromatographic techniques could be used to identify particular species. However extractive techniques would be required for sampling prior to any measurement and thus the stability of the analytes in heated lines is required to be known.

Further research is obviously required into the application of online analysis systems to determine the degradation products and in the absence of such research findings, then some assurance from the marketeers that such systems can determine the selected analytes at the concentration levels expected is required. Whether such research will be funded by the instrument manufacturers, by governments or by the PCC (or fossil fuel) industries is open to debate.

However, if sensitivity or the environmental factors remain as issues, then some novel experimentation will be required – one approach may be to use the smog chamber at CSIRO Lucas Heights e.g. as nitrosamines have a strong absorption at 254 nm and since the chamber’s ozone analyser also measures at 254 nm, it would allow gas phase absorption by nitrosamines to be investigated. The existing sensitivities of the instruments attached to the smog chamber are 0.1 ppbv for the ozone analyser and 0.5 ppbv for the NO_x analyser. Thus, for example, at a concentration of 1 ppmv of MEA in the exhaust duct and with 1% conversion of the MEA to NDEA, the analysers would respond usefully. However, water interference in the NO_x analyser could be a problem and this has not been assessed. Another experimental approach to assess the potential for the emissions to be damaging in the atmosphere would be to sample the exhaust into a “mini smog” chamber equipped with UV lights and suitable analysis equipment (this would possibly include a PTR-MS). This “mini smog” could be configured to represent air parcels down-wind as well as direct sampling of stack. Dark measurements and UV measurements would give equally important results. The air space can be conditioned and sampled using FTIR and mass spectrometric techniques.

If non-commercial online analysis systems were to be used (and the brief for this report was to evaluate only commercially available systems), consideration should be given to use of mass spectrometry e.g. LCMS or GCMS (see Tibbett et al., 2010) in combination with some form of manual sampling (see Azzi et al., 2010).

As mentioned above and also in Azzi et al., 2010, one of the greatest challenges in using CEMs or online analysis systems is the sensitivity of these systems; this is especially so when compared with techniques based on manual sampling and laboratory-based analyses in which the full array of instrumental procedures based on GC and MS instrumentation can be applied. Also, the presence of aqueous aerosol particles may well impact on the use of online analysers (CEMs) for the determination of specific analytes; this is especially so for polar species which are likely to dissolve in these aerosols.

It is thought that on-line analysis systems (CEMs) for the determination of emissions from PCC plants will become available in response to changes to legislation. But at this stage, there is little incentive for manufacturers to develop techniques that may or may not be required in the future for such plants.

5 ACKNOWLEDGEMENTS

The following from CSIRO Energy Technology are thanked for their contribution to this work: Rob Rowland, Stuart Day, Phil Jackson, Paul Feron, David French, Owen Farrell and James McGregor.

6 REFERENCES

Note that all websites listed below and in the text above have been accessed in September, October and November, 2010.

Attalla, M. and Azzi, M. (2010). Environmental Impacts of Emissions from Post Combustion CO_2 Capture at Environmental Impacts of Amine Emission During Post Combustion Capture, 16 February 2010, Oslo, Norway. IEA Greenhouse Gas R&D Programme http://www.ieaghg.org/index.php?/environmental-impacts-of-amine-emission-during-post-combustion-capture.html

Azzi, M, Day, S., French, D., Halliburton, B., Jackson, P., Lavrencic, S. Riley, K. and Tibbett, A. (2010). CO_2 Capture Mongstad - Project A – Establishing sampling and analytical procedures for potentially harmful components from post-combustion amine based CO2 capture, Task 2: Procedures for Manual Sampling, EP 105456, CSIRO, Australia.

Bacon, T., (2002). Ion Mobility Spectroscopy Applications for Continuous Emission Monitoring, Molecular Analytics. http://www.jusun.com.tw/IMS%20Application%20for%20CEM.pdf)

Bacon, AT., Getz, R. and Reategul, J. (1991). "Ion-Mobility Spectrometry Tackles Tough Process Monitoring," Measurement and Control.

Baker, R., Peters, R. and Chikhliwala, E. (2004). Use of Multicomponent Infrared Gas Analyzers at Waste-to-Energy Facilities, presented at 12th Annual North American Waste-to-Energy Conference (NAWTEC 12), Savannah, GA, May 17-19, 2004.

Barber, T.E., Ayala, N.L., Storey, J.M. E., Powell, G.L., Bosey, W.D. and Smyrl, N.R. (2005). Infrared Absorption Spectroscsopy, Chapter 5 in: Down, R.D. and Lehr, J.H., (Eds), Environmental Instrumentation and Analysis Handbook, John Wiley & Sons Inc. 2005, 1068 pages.

Bello, A. and Idem, R. O. (2005). Pathways for the formation of products of the oxidative degradation of CO_2 loaded concentrated aqueous monoethanolamine solutions during CO_2 absorption from flue gases. Ind. Eng. Chem. Res. 2005, 44 (4), 945–969.

Blake, R.S., Monks, P.S. and Ellis, A.M. Proton-Transfer Reaction Mass Spectrometry, Chem. Rev., 2009, 109 (3), 861–896.

Bottoms, R.R., Girdler Corp. (1930). "Separating acid gases," U.S. Patent 178390, cited in Rochelle, (2009).

Evans S., Jahnke, J.A. and Dene, C. (2006). Microsensors for Continuous Emissions Monitoring, EPRI Report 1012694. http://mydocs.epri.com/docs/public/000000000001012694.pdf

Goff, G. S. and Rochelle, G.T. (2004). Monoethanolamine degradation: O_2 mass transfer effects under CO_2 capture conditions. Ind. Eng. Chem. Res., 43 (20), 6400–6408.

Halliburton, B., Day, S., Lavrencic, S., Riley, K. and Azzi, M. (2010). CO_2 Capture Mongstad - Project A – Establishing sampling and analytical procedures for potentially harmful components from post-combustion amine based CO_2 capture. Task 1: Design of Sampling Points for Treated Flue Gas. EP 104693, CSIRO, Australia.

Isacsson, U. and G. Wettermark, G. (1974). Chemiluminescence in analytical chemistry, Analytica Chimica Acta, 68(2), 339-362.

Johnston, J.E. and Baum, M.M. (2005). Ultraviolet Analyzers, Chapter 6 in: Down, R.D. and Lehr, J.H., (Eds), Environmental Instrumentation and Analysis Handbook, John Wiley & Sons Inc. 2005, 1068 pages.

Kamijo, T (2010). MHI Amine Emission Control Technology at Environmental Impacts of Amine Emission During Post Combustion Capture, 16 February 2010, Oslo, Norway. IEA Greenhouse Gas R&D Programme. http://www.ieaghg.org/index.php?/environmental-impacts-of-amine-emission-during-post-combustion-capture.html

Knudsen, S., Karl, M. and Randall, S. (2009) Summary Report: Amine Emissions to Air during Carbon Capture. Phase I: CO_2 and Amines Screening Study for Effects to the Environment. N-108068, Norwegian Institute for Air Research (NILU).

Lindinger, W., Hansel, A. and Jordan, A. (1998). Proton-transfer-reaction mass spectrometry (PTR–MS): on-line monitoring of volatile organic compounds at pptv levels, Chemical Society Reviews, 27, 347-354.

Myers, J., Kelly, T., Lawrie, C. and Riggs, K. (2000). Environmental Technology Verification Report, Unisearch Associates Lasir® Tunable Diode Laser Open-Path Monitor, prepared by Battelle for USEPA. http://www.epa.gov/etv/pubs/01_vr_unisearch.pdf

McGowan, G. (2005). In situ versus extractive measurement techniques, Chapter 2 in: Down, R.D. and Lehr, J.H., (Eds), Environmental Instrumentation and Analysis Handbook, John Wiley & Sons Inc. 2005, 1068 pages.

Nielsen, C.J., D'Anna, B., Dye, C., George, C., Graus, M., Hansel, A., Karl, M., King, S., Musabila, M., Müller, M., Schmidbauer, N., Stenstrøm, Y. and Wisthaler, A. (2010). Atmospheric Degradation of Amines (ADA), Summary Report: Gas phase photo-oxidation of 2-aminoethanol (MEA), CLIMIT project no. 193438.

Pogány, A., Mohácsi, R.P.D., Varga, A., Bozóki, Z., Galbács, Z., Horváth, L. and Szabo, G. (2009). Compact Detector with Sub-ppb Accuracy Using Near-Infrared Photoacoustic Spectroscopy and Preconcentration Sampling. Environmental Science and Technology, 43 (3), 826–830

Rintekno, (2010). Amine Emissions and Monitoring, Report on WTO nr 24 (Open version) to GASSNOVA (Kårstø), Nr. RF0041U-100A-001.

Rochelle, G.T. (2009). Amine Scrubbing for CO_2 Capture, Science, 325 (5948), 1652-1654.

Sander, R., (1999). Compilation of Henry's Law Constants for Inorganic and Organic Species of Potential Importance in Environmental Chemistry (Version 3) http://www.henrys-law.org

Shao, R. and Stangeland, A., (2009). Amines Used in CO2 Capture - Health and Environmental Impacts, Bellona Report, September 2009.

Sloss, L. (1997). Continuous emissions monitoring for coal-fired power stations. IEACR/94, IEA Coal Research, London, UK.

Svendsen PT. (Ed.) (2007). Carbon Capture and Storage at Kåarstø. Norwegian Water Resources and Energy Directorate (NVE). http://www.nve.no/global/publikasjoner/publikasjoner%202007/report%202007/nvereport%202-07_b.pdf

Tibbett, A., Day, S and Azzi, M. (2010). CO_2 Capture Mongstad - Project A – Establishing sampling and analytical procedures for potentially harmful components from post-combustion amine based CO_2 capture. Task 4: Literature Survey of Analytical Procedures and Recommendations; EP 105542, CSIRO, Australia.

United States Department of Labour, Occupational Safety and Health Administration. http://www.osha.gov/

United States Environmental Protection Agency (2000), ETV Advanced Monitoring Systems Center, Myers, J., Kelly, T., Lawrie, C. and Riggs, K., Environmental Technology Verification Report on UNISEARCH Associates LasIR® Tunable Diode Laser Open-Path Monitor, Battelle, Columbus, Ohio 43201, USA. http://www.epa.gov/etv/pubs/01_vr_unisearch.pdf

United States Environmental Protection Agency, (1997). Handbook - Continuous Emission Monitoring Systems for Non-criteria Pollutants, EPA/6251R-971001, 169 pages. http://www.epa.gov/nrmrl/pubs/625r97001/625r97001.pdf

United States Environmental Protection Agency, (1984).Method TO-1 (Revision 1.0), Method for the determination of volatile organic compounds in ambient air using tenax® adsorption and gas chromatography/mass spectrometry (GC/MS).

United States Environmental Protection Agency, (1984). Method TO-5 Revision 1.0. Method for the determination of aldehydes and ketones in ambient air using high performance liquid chromatography (HPLC). http://www.epa.gov/ttn/amtic/files/ambient/airtox/to-5.pdf

United States Environmental Protection Agency, (1999). Method TO-11A, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air (Second Edition) Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC), Center for Environmental Research Information Office of Research and Development, EPA/625/R-96/010b. http://www.epa.gov/ttn/amtic/files/ambient/airtox/to-11ar.pdf

United States Environmental Protection Agency, (1999). Method TO-16 (2nd Edition) - Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Long-Path Open-Path Fourier Transform Infrared Monitoring of Atmospheric Gases, EPA/625/R-96/010b.

United States Environmental Protection Agency, Method TO 17, Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling onto Sorbent Tubes, EPA/625/R-96/010b, 49 pages.

United States Environmental Protection Agency (2009), Method 7E—Determination of Nitrogen Oxides Emissions from Stationary Sources (Instrumental Analyzer Procedure). http://www.epa.gov/ttn/emc/promgate/method7E.pdf

United States Environmental Protection Agency, Method 18 - Measurement of Gaseous Organic Compound Emissions by Gas Chromatography. http://www.epa.gov/ttn/emc/methods/method18.html

United States Environmental Protection Agency Method 202 - Determination of Condensible Particulate Emissions from Stationary Sources http://www.epa.gov/ttn/emc/promgate/m-202.pdf

United States Environmental Protection Agency (1999). Method 320, Measurement of Vapor Phase Organic And Inorganic Emissions by Extractive Fourier Transform Infrared (FTIR) Spectroscopy. http://www.epa.gov/ttn/emc/methods/method320.html

United States Environmental Protection Agency (2004). Revised Environmental Technology Verification Report on the OPSIS AB LD500 Continuous Emission Monitor for Ammonia. http://www.epa.gov/etv/pubs/01_vr_opsis_ld500.pdf

United States Environmental Protection Agency Technology Transfer Network Emission Measurement Center, http://www.epa.gov/ttnemc01/

United States Environmental Protection Agency, Technology Transfer Network, Emission Measurement Center, CFR Promulgated Test Methods (TM). http://www.epa.gov/ttn/emc/promgate.html

Veltman, K., Singh, B. and Hertwich, E.G. (2010). Human and Environmental Impact Assessment of Postcombustion CO_2 Capture Focusing on Emissions from Amine-Based Scrubbing Solvents to Air, Environmental Science & Technology, 44(4),1496-1502.

Wada, E.T. and Sterling, A.M. (2001). Development and evaluation of a mass spectrometer-based continuous emission monitor for volatile organic compound emissions from combustion devices. Waste Management, 21(5), 477-482.

APPENDIX: ANALYTES

The analytes listed in Table 1 as well as ammonia and some of the solvent amines may or may not be present in the exhaust duct of the amine based carbon capture plant to be built at Monstad but they are possible degradation products from such a system and as such as discussed below. The sampling regime has been discussed in the reports of Tasks 1 and 2 (Halliburton et al., 2010 and Azzi et al., 2010) and the analytical techniques that could be applied to a range of samples taken from the plant (not only the exhaust gas) are detailed in the report of Task 4 (Tibbett et al., 2010). The findings in these reports are generally applicable in the discussions in this report. Some of the information in the following sub-sections (A.1–A.6) may be found in greater detail in Tibbett et al., (2010).

Standards detailing methods of analysis for many of the analytes listed in Table 1. are methods of the US institutions such the California Air Resources Board (CARB), the Occupational Health and Safety Administration (OSHA) and the National Institute for Occupational Safety and Health (NIOSH), the Food and Drug Administration (FDA), the International American Society for Testing and Materials (ASTM) and the Environmental Protection Agency (USEPA) as well as United States Department of Labour, Occupational Safety and Health Administration. Other bodies such as the various standards bodies of individual countries and the International Organization for Standardization provide details of methods of analysis for the analytes listed in Table 1. Some of these bodies also provide details of online analysers or CEMs.

In the following sections are brief details of the various methods applicable to the analysis of the various species of interest to the operators of amine-based carbon capture plants.

A.1 Aldehydes

The aldehydes listed in Table 1 are formaldehyde and acetaldehyde. On the World Health Organisation’s (WHO) International Agency for Research on Cancer (IARC) lists, formaldehyde is identified as a Group 1 carcinogen and acetaldehyde as a Group 2A probable carcinogen. Thus, not surprisingly, there are “standard” methods for the determination of carbonyls in air; these are USEPA Method TO-5 and Method TO-11A (specifically for formaldehyde but at least 14 other carbonyl compounds can be quantified). The detection limit quoted for Method TO-5 is 1-2 ppbv. Whereas, in the later Method TO-11A, a procedure for the determination of the “method detection limit” is given but it is stated that the method “can be used for long-term (1-24 hr) sampling of ambient air where the concentration of formaldehyde is generally in the low ppb (v/v) or for short-term (5-60 min) sampling of source-impacted atmospheres where the concentration of formaldehyde could reach the ppm (v/v) levels”. Both methods are based on the derivitisation of carbonyls with dinitrophenylhydrazine (DNPH) and the measurement of the intensity of the colour at 360-370 nm UV by HPLC (see Figure A.1).

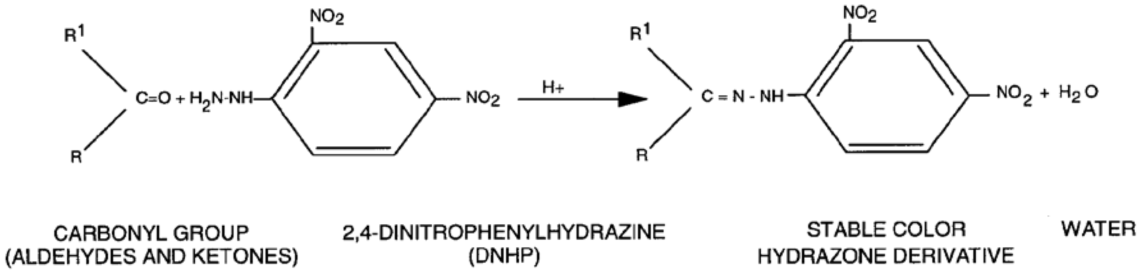

Figure A.1. Reaction of Carbonyls with DNPH.

According to Tibbett et al., 2010, derivatisation with DNPH is recommended for the determination of formaldehdye and acetaldehyde in both gaseous and liquid samples from amine-based PCC plants. “The recommended guidance is US EPA Method 0011 and CARB 430 for collection of gas phase samples from stationary source emissions using an impinger charged with the DNPH liquid or a DNPH sorbent cartridge. US EPA Method 8315A is recommended for analysis of impinger collected samples or Method 524 for collection of liquid samples for DNPH treatment and SPE concentration. All methodologies use HPLC analysis with UV detection. A superior detector is diode array (DAD) and this is recommended to provide a level of conformational information. The procedural minimum detection limit (MDL) in the gas phase is expected to be 0.15 µg/m^3 (0.12 ppbv as formaldehdye) using nominal 100L gas sampling volume; and in the liquid phase; 0.3 µg/L.”

At this stage, there are no commercially available CEM systems for the determination of formaldehyde and acetaldehyde in exhaust ducts and it is doubtful that it will be possible to determine these compounds by such systems in the near future. CEMs are frequently used for other analytes but not the aldehydes.

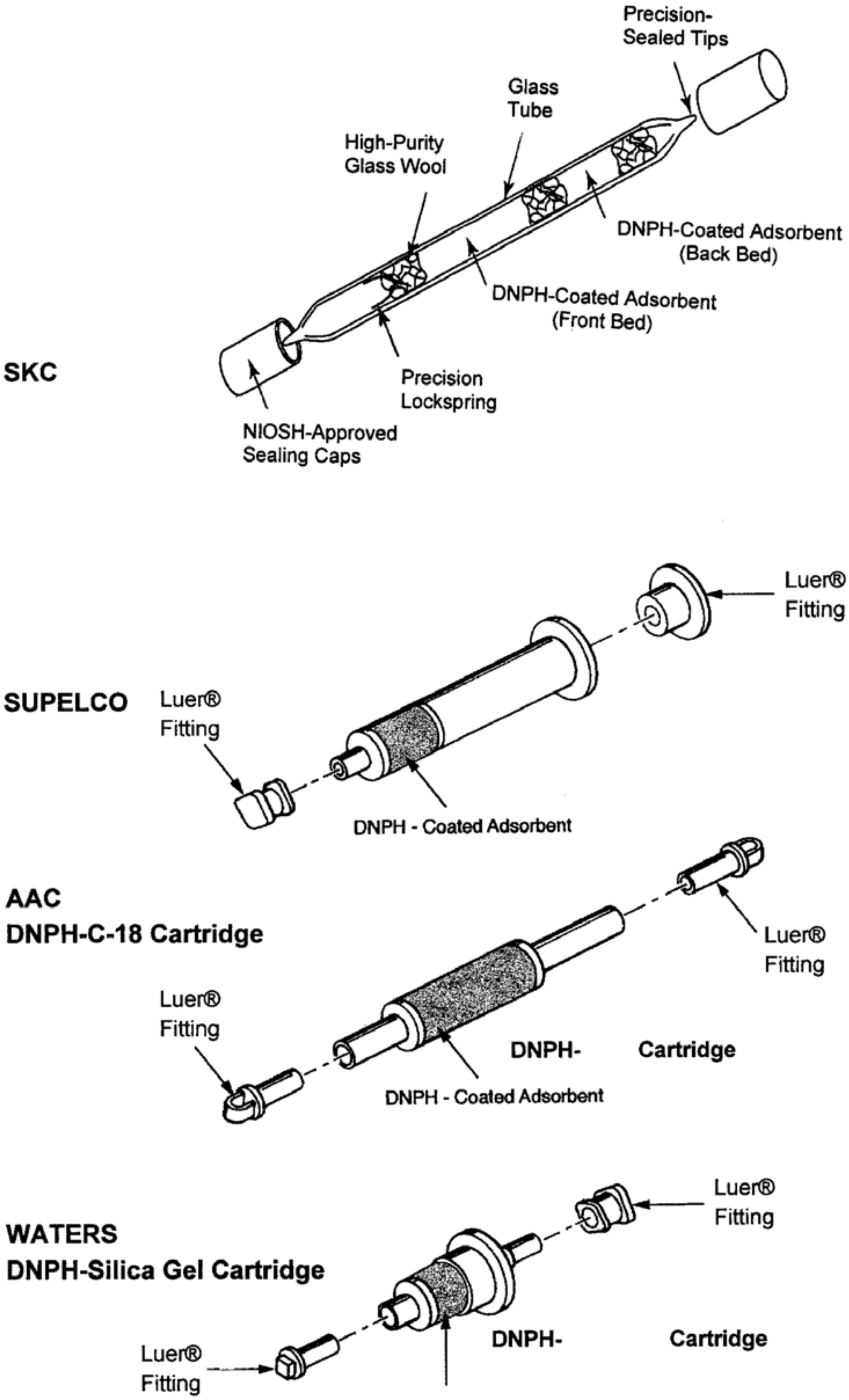

Figure A.2. Examples of Commercially Available DNPH-Coated Cartridges (copyright USEPA).

Although carbonyls are very reactive, continuous emissions monitoring of formaldehyde is possible but probably cannot achieve the sensitivity required by CCM.

An application note (by LumaSense), “Monitoring Formaldehyde in a Chipboard Manufacturing Plant” describes the use of a multi-gas monitor, which works on the basis of photoacoustic measurement (PAS) of the infrared spectrum and has been used to monitor the emissions of formaldehyde to a detection limit of 0.04 ppmv, as well as other gases including total organic carbon (TOC) down to the same concentration. The web address is: http://www.lumasenseinc.com/uploads/LumaSense/PDF/Environment/Aplic_Formaldehyde_Chipboard.pdf . However this concentration level is probably too high for that expected at the CCM plant where the level of carbonyl compounds is expected to be in the low ppbv range. It is noted that the system can also be used to measure acetaldehyde.

A.2 Amines (includes akylamines and alkanolamines)

According to Tibbett et al., (2010), there are standard methods suitable for the majority of the compounds targeted by the developers of the CCM project (see Table 1), “with the exception of N-methyldiethanolamine. Inclusion of this compound is likely possible into the target suite. The “methods are all applicable to gas phase collection and limited standard methods exist for their analysis in the liquid phase”. Contrary to the impression gained by number of standard methods available, Fekete et al., (2010) state that the measurement of amines in environmental samples is challenging as these compounds are highly polar and their isolation and chromatographic determination are or can be difficult.

There are CEM systems that can be used to monitor amines. In Australia (and presumably other places where amine-based PCC pilot plants are being studied) amines are currently being estimated in emissions by FTIR techniques. It should be restated that the amines from the solvent are likely to be present at much greater concentrations than that of any degradation product formed.

A.3 Amides

The amides of interest are formamide and acetamide (Table 1). Tibbet et al., (2010) note that under current regulations, the monitoring of these compounds is “not a major priority nor are they emerging as contaminants of high importance” Thus, there are few established offline analytical methods. There are methods from OHSA that use “rudimentary collection procedures”. GC/NPD is specified but GC/MS (with some loss of sensitivity) would be preferable for samples obtained from the CCM plant. Methods would require development. It is stated by Tibbett et al., (2010) that “GC analysis is an option” and that the collection on a sorbent and subsequent “thermal desorption is an attractive option for gas phase samples”. Further comment made by the authors is that “MS detection is preferable to other detectors for reasons of confirmation in mixed amine and amide matrices” and that chemiluminescence detection after chromatography should be considered. Because these compounds are polar, HPLC may be useful and that LC/MS could be used for liquid samples.The authors state that “Significant development would be required.....if these compounds were to remain a priority”.

There seems to be no commercially available online methods of analysis for these amides in exhaust ducts at low levels (i.e. if they are present in the exhaust duct of the CCM plant). It would seem to be feasible to sorb these species onto an appropriate reagent and then thermally desorb the species. Although not continuous, it would be one way of creating an online system that could be applied to CCM.

Although as mentioned above, an application note, “Monitoring Formaldehyde in a Chipboard Manufacturing Plant” describes the use of a multi-gas monitor; this system works on the basis of photoacoustic measurement (PAS) of the infrared spectrum and has been used to monitor the emissions of formaldehyde to a detection limit of 0.04 ppmv, as well as other gases including total organic carbon (TOC) down to the same concentration.

A.4 Ammonia

There are standard methods used for the determination of ammonia in gas samples (e.g. the Japanese Industrial Standard (2004), JIS Method K 0099 for flue gas in which an impinger is used to collect the analyte into a solution of boric acid, which subsequently can be measured by spectrophotometry or ion chromatography, IC and the OSHA Method ID-188, in which the gas is collected using carbon bead/sulphuric acid impregnated sampling tubes; meaurement is also by IC). Procedural method detection limits (MDL) are given in Tibbett et al., (2010). Recently, Benson et al., (2010) have reported on the use of a chemical ionization mass spectrometer for ambient measurements of ammonia in samples from the atmosphere. Whether mass spectrometry could be applied to the online sampling and analysis of the emissions an exhaust duct is worthy of further study.

There are two suitable CEMs listed in USEPA Environmental Technology Verification Program; these are:

- OPSIS AB LD500 continuous emission monitor for ammonia; http://www.epa.gov/etv/pubs/01_vr_opsis_ld500.pdf
- Siemens Laser Analytics AB LDS 3000 continuous emission monitor for ammonia; http://www.epa.gov/etv/pubs/01_vr_siemens.pdf

There are reports on both instruments on the AMS website and these include brief descriptions of the operating systems, e.g.

“The OPSDIS LD500 system is an optical open-path monitoring system designed to measure ammonia, water vapour, hydrochloric acid, hydrogen fluoride, oxygen, and temperature. It can be configured with up to eight individual paths. A total of four laser diode heads can be installed, each one a complete laser control and data sampling system monitoring a specific gas” and “The LDS 3000 is designed to measure gases in situ and in real time in harsh environments and to provide dynamic dust load compensation, interference-free operation, and minimized maintenance by means of a patented built-in calibration system” and also “Second derivative spectroscopy is used to enhance resolution and immunity against hostile environments (flames, etc.) and minimize zero and span drift. The LDS 3000 uses the light emitted from a semiconductor laser tuned over a single absorption line of the gas to be measured. The light is split into five paths using a passive optical splitter. One, two, or three paths are used for the measurement channels. Two internal paths are used for internal checks of the laser: one is used to monitor the laser power and one is used in an internal measurement path”.

Related to the measurement of NH_3 by CEM systems is the research of von Bobrutzki et al., 2010. The researchers looked at 11 different techniques to measure ambient concentrations of the analyte. Some of the findings stated by these researchers were:

- inlet length to detectors and the frequency at which filters should be changed
- “instruments based on chemical ionisation mass spectroscopy and quantum cascade laser absorption spectroscopy need to be calibrated or at least zeroed frequently”

- wet chemical techniques had good long-term stability and could be used to reliably differentiate between gas phase NH_3 and aerosol NH_4^+
- some instrument are not suitable at <1ppbv and ion mobility spectroscopy was limited to <20ppb

The researchers concluded that "Despite, recent advances in technologies, the continuous measurement of NH_3 remains a challenging and costly enterprise...".

It is apparent that online systems of measuring ammonia do require careful consideration before installation in some environments. The presence of aqueous aerosol particles in the exhaust duct of the CCM plant is a factor that must be considered when online systems are used for the determination of polar compounds including ammonia.

A.6 N-nitrosamines

There are standard methods (i.e. established by international and national institutions e.g. USEPA, NIOSH) applicable to many of the N- nitrosamine compounds identified as being of interest to the operators of the CCM plant; this is especially so for those deemed to be volatile (NMEA, NDEA, NMor, NPip) and also to one non-volatile compound (NDELA) in ambient air and water, There appears to be no standard methods for the compounds, N -nitrosopiperazine and 1,4-dinitrosopiperazine. However "it is considered that these would be applicable for determination using these methods" (Tibbet et al., 2010), after some development and subsequent validation. Tibbett et al., (2010) state that "gas chromatographic (GC) based methods may not provide the necessary resolution for these more polar species and liquid chromatography (LC) would be evaluated as a more viable alternative".

If not available commercially, it may be possible to develop CEM systems and these may be adapted from some of these methods discussed by Tibbett et al., (2010). Sensitivity of CEM or online analytical techniques is still a challenge.

A.7 Bibliography for Appendix

Note that all websites listed below and in the appendix above have been accessed in September, October and November, 2010.

Azzi, M, Day, S., French, D., Halliburton, B., Jackson, P., Lavrencic, S. Riley, K. and Tibbett, A. (2010). CO_2 Capture Mongstad - Project A – Establishing sampling and analytical procedures for potentially harmful components from post-combustion amine based CO2 capture, Task 2: Procedures for Manual Sampling, EP 105456, CSIRO, Australia.

Benson, D.R., Markovich, A., Al-Refai, M. and Lee, S.-H., (2010). A Chemical Ionization Mass Spectrometer for ambient measurements of Ammonia. Atmospheric Measurement Techniques, 3, 1075–1087.

von Bobrutzki, K., Braban, F., Famulari, D., S. K. Jones, S.K., Blackall, T., T. E. L. Smith, T.E.L, Blom, M., H. Coe, M., Gallagher, M., Ghalaieny, M., McGillen, M.R., Percival, C.J., Whitehead, J.D., Ellis R., J. Murphy, J., Mohacsi, A., Pogany A., Junninen, H., Rantanen, S., M. A. Sutton, M.A., and Nemitz, E. (2010). Field inter-comparison of eleven atmospheric ammonia measurement techniques, Atmospheric Measurement Techniques, 3, 91–112.

Fekete, A., Malik, A.K., Kumar, A. and Schmitt-Koppin, P. (2010). Amines in the environment, Critical Reviews in Analytical Chemistry, 40, 102-121.

Halliburton, B., Day, S., Lavrencic, S., Riley, K. and Azzi, M. (2010). CO_2 Capture Mongstad - Project A – Establishing sampling and analytical procedures for potentially harmful components from post-combustion amine based CO_2 capture. Task 1: Design of Sampling Points for Treated Flue Gas. EP 104693, CSIRO, Australia.

Japanese Industrial Standard, (2004). JIS Method K 0099: Methods for the Determination of Ammonia in Flue Gas. JSA Publications, Japan.

Tibbett, A., Day, S and Azzi, M. (2010). CO_2 Capture Mongstad - Project A – Establishing sampling and analytical procedures for potentially harmful components from post-combustion amine based CO_2 capture. Task 4: Literature Survey of Analytical Procedures and Recommendations; EP 105542, CSIRO, Australia.

United States Environmental Protection Agency, (1984).Method TO-1 (Revision 1.0), Method for the determination of volatile organic compounds in ambient air using tenax® adsorption and gas chromatography/mass spectrometry (GC/MS).

United States Environmental Protection Agency, (1984). USEPA Method TO-5 Revision 1.0. Method for the determination of aldehydes and ketones in ambient air using high performance liquid chromatography (HPLC).
http://www.epa.gov/ttn/amtic/files/ambient/airtox/to-5.pdf

United States Environmental Protection Agency, Technology Transfer Network, Emission Measurement Center, CFR Promulgated Test Methods (TM).
http://www.epa.gov/ttn/emc/promgate.html

United States Environmental Protection Agency, (1997). Handbook - Continuous Emission Monitoring Systems for Non-criteria Pollutants, EPA/6251R-971001, 169 pages.
http://www.epa.gov/nrmrl/pubs/625r97001/625r97001.pdf

United States Environmental Protection Agency (1999) Test Method 320, Measurement of Vapor Phase Organic And Inorganic Emissions by Extractive Fourier Transform Infrared (FTIR) Spectroscopy. http://www.epa.gov/ttn/emc/methods/method320.html

United States Environmental Protection Agency, (1999). USEPA Method TO-11A, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air (Second Edition) Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC), Center for Environmental Research Information Office of Research and Development, EPA/625/R-96/010b.
http://www.epa.gov/ttn/amtic/files/ambient/airtox/to-11ar.pdf

United States Environmental Protection Agency, (1999). Method TO-16 (2nd Edition) - Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Long-Path Open-Path Fourier Transform Infrared Monitoring of Atmospheric Gases, EPA/625/R-96/010b.

United States Environmental Protection Agency Technology Transfer Network Emission Measurement Center, http://www.epa.gov/ttnemc01/

United States Environmental Protection Agency (2000), ETV Advanced Monitoring Systems Center, Myers, J., Kelly, T., Lawrie, C. and Riggs, K., Environmental Technology Verification Report on UNISEARCH Associates LasIR® Tunable Diode Laser Open-Path Monitor, Battelle, Columbus, Ohio 43201, USA. http://www.epa.gov/etv/pubs/01_vr_unisearch.pdf

United States Environmental Protection Agency (2009), Method 7E—Determination of Nitrogen Oxides Emissions from Stationary Sources (Instrumental Analyzer Procedure). http://www.epa.gov/ttn/emc/promgate/method7E.pdf

United States Environmental Protection Agency, Method 18 - Measurement of Gaseous Organic Compound Emissions by Gas Chromatography. http://www.epa.gov/ttn/emc/methods/method18.html

United States Environmental Protection Agency (2004). Revised Environmental Technology Verification Report on the OPSIS AB LD500 Continuous Emission Monitor for Ammonia. http://www.epa.gov/etv/pubs/01_vr_opsis_ld500.pdf

United States Environmental Protection Agency, Method TO 17, Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling onto Sorbent Tubes, EPA/625/R-96/010b, 49 pages.

United States Environmental Protection Agency Method 202 - Determination of Condensible Particulate Emissions from Stationary Sources http://www.epa.gov/ttn/emc/promgate/m-202.pdf

United States Department of Labour, Occupational Safety and Health Administration. http://www.osha.gov/

United States Environmental Protection Agency (2004). Revised Environmental Technology Verification Report on the OPSIS AB LD500 Continuous Emission Monitor for Ammonia. http://www.epa.gov/etv/pubs/01_vr_opsis_ld500.pdf