21GRD06 MetCCUS

GOOD PRACTICE GUIDE FOR THE MEASUREMENT OF NITROSAMINES IN POST-COMBUSTION FLUE GAS IN ORDER TO ENABLE THE DIRECT DETERMINATION OF EMISSIONS OF CO2 AND TO ADDRESS THE MEASUREMENT OF AIR POLLUTANTS RESULTING FROM THE CAPTURE PROCESS, SUCH AS DEGRADATION PRODUCTS FROM CAPTURE SOLVENTS

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Organisation name of the lead participant for the deliverable:

National Physical Laboratory

H. Barros, R. Harvey, H. Cheales-Norman,
C. Dimopoulos, R. Robinson (NPL).
C Anderson (ForceTechnology)

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METROLOGY PARTNERSHIP EURAMET

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H. Barros, R. Harvey, H. Cheales-Norman,
C. Dimopoulos, R. Robinson (NPL).
C Anderson (ForceTechnology)

Glossary

CCUS – Carbon Capture Usage and Storage

PCC - Post-combustion Carbon Capture

AMS - Automated measuring system

CEMS - Continuous Emission Measurement System

FTIR - Fourier Transform Infra-Red Spectroscopy

GC-MS – Gas Chromatography Mass Spectrometry

GC-TEA – Gas Chromatography Thermal Energy Analysis

PTR-TOF-MS - Proton Transfer Reaction Time Of Flight Mass Spectroscopy

SIFT-MS - Selected Ion Flow Mass Spectroscopy

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1 Summary

CO_2 capture could contribute significantly to achieve emissions neutrality, reducing existing greenhouse gases inputs from industrial processes and compensating for residual emissions that are hard to eliminate. Amine-based Post-combustion Carbon Capture (PCC) is the most widely used technology in this area. However, toxic degradation products of the CO_2 scrubber amines (as amines, nitrosamines, etc.) are potentially emitted to the atmosphere, impacting health and environment.

This report forms a part of the project EURAMET / METCCUS and is addressing the activity 2.1, Task 2.1.6. (Deliverable 3) scoped to provide guidance on volatile nitrosamines monitoring in PCC plants. This document refers to the requirements proposed in the Task 2.1.1 (Annex 1) and to the method proposed in the Task 2.1.2 (Annex 2), intended for monitoring nitrosamines emissions from the stacks (exhausts) of PCC plants utilizing amine-based solvents as the carbon capture medium. Although this document provides guidance on PCC nitrosamines monitoring emissions, potentially most of the content can be of use for amines monitoring as well. It is worth mentioning that the performance of the proposed method has been demonstrated in Taks 2.1.4 (Annex 3) for a selected group of volatile nitrosamines with vapour pressures ranging 0.005 – 0.4 kPa @ 1 atm and 20 ºC.

In post combustion CO_2 capture plants, the conditions of the flue gas matrix, its composition and particularly the breakdown products originated by the reactions between the amine-based scrubber and the post combustion exhaust gas, present several specific challenges. This means that "traditional" monitoring approaches and methods – both instrumental and manual – may not be suitable to monitor the target pollutants and surely may require modifications.

This guide identifies available manual or continuous emissions (instrumental) monitoring methods for the emerging pollutants (nitrosamines and amines) potentially emitted by PCC plants. When possible, performance characteristics are presented as well as suggested sampling durations. The guide also identifies limitations and adjustments required to the methods (where relevant) due to the unique PCC flue gas characteristics of PCC plants flue gas. It is worth noting that the methods identified for the measurement of nitrosamines (and amines), have not been fully validated for the monitoring (sampling and measurement) of these pollutants. Therefore, currently any result from any of these methods is subject to a large amount of unquantifiable uncertainty. Finally, two different IR-based instruments have been assessed to measure post-capture CO_2 concentrations in simulated PCC stack conditions (Task 2.1.5 in the Annex 4).

It is important to note that PCC emissions is a relatively new area within stack emissions monitoring, featured by a number of challenges linked to a relatively long list of new species that have not been traditionally measured in industrial stacks, including toxic and/or carcinogenic species. In addition, these pollutants are found within a non-typical gas matrix where complex multi-phase transport / emission is taking place. This document recognises that in addition to the development of new methods more validation and research is required, in order to meet the challenges posed by PCC stack emissions. Areas where more research is required are mentioned within this guide.

2 Introduction

Due to the lack of standardised and fully validated methods, this guide focuses on monitoring methods for Post Combustion Carbon Capture Plants (PCC) emissions of amine-based solvent breakdown products and draws information from science deliverables produced under National Physical Laboratory led projects. The method proposed here has been adapted to be applicable to the unique characteristics of PCC plant stack gases.

In general, monitoring flue gas emissions from industrial stationary sources is well established and is carried out following reference methods, the validation of which is required by CEN/TC 264 'Air Quality' as they underpin legislation. These methods can be categorised into either instrumental or manual methods.

Instrumental methods are based on different techniques and designs. They are divided into two main categories, extractive and in situ and can be used for both periodic measurements and as Continuous Emission Measurement Systems (CEMS) permanently mounted on stacks. Typically, periodic measurements are carried out through extractive systems. These continuously extract a sample from the flue gas and deliver it through a sampling system into one or more analysers. Different designs of sampling systems are used (hot and wet, cold, and dry or dilution) depending on the compound being measured and/or the type of analytical technique. The sampling system should deliver the sample gas with its composition

unchanged to the analyser and depending on the type of analyser technique used at appropriate conditions, e.g., temperature, pressure, and flow. Instrumental techniques have the benefit of providing results for a variety of compounds in real time.

In manual methods a sample is extracted from the flue gas, passed through sample media which capture the compound being measured which is then recovered for "offline" analysis in a laboratory. A commonly used technique for measuring gas phase pollutants, is the wet chemistry technique in which the flue gas sample is extracted through a heated sampling system before drawn by a pump through a series of absorbers with trapping solution. The solution used is dependent on the compound to be measured (although this kind of method may be not applicable to all the targeted PCC amine breakdown products). A filter may also be added to the system to collect any particulates for further analysis and/or to protect the downstream sampling system from particulates.

3 Flue gas physical properties and composition

Stack conditions in amine-based PCC exhausts are unlike most other combustion exhausts. The gas temperature is usually around 40 – 50 °C which is significantly lower than typical combustion flue gas temperatures. This means the gas is likely to be saturated as the hot combustion gas is cooled below dew point. Additionally, there is the potential for water/solvent to be present in droplet form. This can lead to super saturated conditions with larger droplets of the amine-based solvent suspended in a matrix of saturated combustion gas.

Studies [1,2,3] have also shown that aerosols tend to form in the flue gas. Solid (soot, H2SO4 and salts) and liquid (vapourised water, ammonia and HCl) particles act as aerosols coagulation/condensation nuclei, while absorption of amines and nitrosamines onto the aerosols suspended within the flue gas is a significant discharge route. Amine emissions seem to be proportional to the aerosol particle number concentration [4,5]. No method is currently widely available to measure aerosol particle number concentration from PCC plants.

The bulk chemical composition of the stack gas will depend on the process exhaust feeding the carbon capture process. Apart from reducing the CO_2 content, the carbon capture process itself has the potential to alter the composition and relative concentrations of the flue gas components.

There is a potential for the release of the solvent itself – commonly monoethanolamine (MEA). Reactions between the combustion exhaust gas and amines in the solvent can also produce a suite of secondary breakthrough by-products – secondary and tertiary amines, nitrosated amines (nitrosamines), nitramines, and ammonia, mainly via oxidation reactions and thermal degradation. Most nitrosamines are known to be toxic, mutagenic, and/or carcinogenic.

Several factors affect the rate of breakdown of the amine-based solvent including the age of the solvent, nitrogen oxide levels in the stack gas, metal particles (from corrosion), sulphur compounds, oxygen levels in the stack gas and temperature.

4 Monitoring of PCC nitrosamine emissions

4.1 Manual extractive sampling

The presence of liquid aerosol or solid particles in the flue gas means that the distribution of soluble or reactive pollutant species within the duct must be assumed to be inhomogeneous. Also, it implies that low volatility, but soluble/reactive pollutants can be transported by water droplets (or fine particles) and then can be potentially emitted from PCC stacks (see section 2 of MetCCUS Task 2.1.1 report). Therefore, best practice to perform manual extractive testing consists in isokinetic sampling (i.e. sampling at a flow rate such that the velocity entering the sampling system is the same as the velocity of the flue gas at the measurement point) at multiple points across the duct (grid sampling), according to the requirements of BS EN 13284-1 [6]. In cases where the moisture level of the bulk gas is below saturation point, droplets of the solvent may still be present.

The potential for thermal breakdown of the amine-based solvent should also be considered when sampling for breakdown products. Thermal degradation of some target species in the PCC stripper unit has been noted to occur from 120°C upwards. The heated elements within a manual extractive sample system (probe, filter, heated sampling lines) are typically operated above this temperature (150 - 180°C depending on the monitoring method) to prevent condensation and sample loss within the sample system. In order to prevent thermal degradation in the sample train, the best practice to sample breakdown products is maintaining the heated elements of the sampling system below 120°C. During field trials the results of which have been used to develop this guide, a temperature of 80°C was used [16]. The selected temperature is low enough to eliminate the risk of any "hot spots" within the heated elements of the sampling system that would lead to thermal degradation of the sample, but also above the stack gas temperature and so prevents further condensation in the sample system.

For volatile nitrosamines, there has been developed and tested a manual absorber method, described in the MetCCUS Task 2.1.2 report. As far as we know, this is the only method for which validation data is available [16, 18].

4.2 Instrumental sampling

As part of the best practices, a stack gas homogeneity test should be carried out according to the requirements of BS EN 15259 [7] and in the UK additional guidance is presented in the associated Method Implementation Document (MID) for 15259 [8]. The MID does not normally require a homogeneity test for ducts with a cross-sectional area less than $1m^2$. Given the nature of the stack gas and the high probability of the presence of droplets, it is strongly recommended that the test is carried out on all stacks, regardless of the cross-sectional area value.

There are no specific requirements relating to sampling in saturated ducts in instrumental monitoring standards, with the following exceptions:

- CEN TS 17337:2019 [9] (monitoring using an FTIR) states that sample gas should be extracted isokinetically when droplets are present in the stack gas.
- CEN TS 17021:2017 [10] (monitoring SO_2) states that if there are droplets present it should be discussed with the local competent authority if the method is suitable.

This guide recommends as best practice that instrumental methods be implemented isokinetically.

Since there are no standard methods for CEMS in PCC stacks conditions, neither for the amines breakdown products already observed in PCC (particularly nitrosamines), the use of this kind of methods for monitoring purposes should be validated beforehand.

4.3 Volatile nitrosamine species in PCC

Nitrosamine emissions from PCC plants arise from the amine-based solvent breakdown and reactions with the combustion gases. Breakdown products of the amine-based capture solvent include secondary and tertiary amines, nitrosamines, and nitramines (among other compounds).

Table 1 summarises the nitrosamines with vapour pressures between 0.001 and 0.4 kPa, which has been reported as measured in PCC plants (either in the scrubber solutions, the water-wash, and/or the emissions).

Table 1 highlight the volatile nitrosamine species, for which the manual stack monitoring method described in the Task 2.1.2 report applies. On the other hand, Table 2 lists the nitrosamine species having lower volatility, for which further research is required to propose, test and validate sampling and monitoring methods.

The difficulty related to the sampling and measurement of the nitrosamines listed in Table 2 not only depends in their low volatility, but also in the fact that many of these nitrosamines have also additional functional groups conferring to them different properties. For instance, five of these nine nitrosamine species are also alcohols.

Table 1. Nitrosamines found in PCC with vapour pressures between 0.002 and 0.4 kPa.

Structure	Mass	Formula	CAS	Nitrosamine compound	Acronym
Linear	74	C2H6N2O	62-75-9	Nitrosodimethylamine	NDMA
Linear	88	C3H8N2O	10595-95-6	Nitrosomethylethylamine	NMEA
Linear	102	C4H10N2O3	55-18-5	Nitrosodiethylamine	NDEA
Linear	130	C6H14N2O	601-77-4	Nitrosodiisopropylamine	NDIPA
Linear	130	C6H14N2O	621-64-7	Nitrosodipropylamine	NDPA
Ring (6)	114	C5H10N2O	100-75-4	Nitrosopiperidine	NPIP
Ring (5)	116	C4H8N2O2	39884-53-2	Nitroso-2-methyloxazolidine	NMOx
Ring (5)	100	C4H8N2O	930-55-2	Nitrosopyrrolidine	NPYR
Linear	158	C8H18N2O	924-16-3	Nitrosodibutylamine	NDBA
Linear	158	C8H18N2O	997-95-5	Nitrosodiisobutylamine	NDIBA
Ring (6)	116	C4H8N2O2	59-89-2	Nitrosomorpholine	NMOR
Ring (6)	115	C4H9N3O	5632-47-3	Nitrosopiperazine	MNPZ*

Notes: * MNPZ is a nitrosamine and also an amine.
All the listed compounds are secondary nitrosamines.

Table 2. Nitrosamines found in PCC with vapour pressures between below 0.002 kPa.

Other functional groups	Structure	Mass	Formula	CAS	Nitrosamine compound	Acronym
Alcohol	Linear	118	$C_4H_{10}N_2O_2$	13147-25-6	Ethylethanolnitrosamine	EHEN
Alcohol	Linear	104	$C_3H_8N_2O_2$	26921-68-6	2-Methylnitrosoaminoethanol	NMELA
Alcohol x 2	Linear	134	$C_4H_{10}N_2O_3$	1116-54-7	Nitrosodiethanolamine	NDELA
-	Ring (6)	114	$C_4H_8N_4O_2$	140-79-4	Dinitrosopiperazine	DNPZ
Glycine Alcohol	Linear	148	$C_4H_8N_2O_4$	80556-89-4	Nitroso-2-hydroxyethyl-glycine	N-HEGly
-	Ring(6)x2	226	$C_{14}H_{14}N_2O$	5336-53-8	N-nitrosodibenzylamine	NDBzA
-	Linear	299	$C_{18}H_{38}N_2O$	1207995-62-7	N,N-bis(3,5,5-trimethylhexyl)nitrous amide	NDiNA
Alcohol	Ring (6)	159	$C_6H_{13}N_3O_2$	48121-20-6	4-Nitroso-1-piperazineethanol	-
Nitramine	Ring (6)	160	$C_4H_8N_4O_3$	107938-05-6	1-Nitro-4-nitrosopiperazine	-

On the other hand, currently, it has been observed limited analytical capabilities for the specific nitrosamine species potentially emitted from PCC stacks with appropriate Limits of Detection (LODs). This limited capability has been also observed in relation to the sample matrices obtained by PCC manual stack sampling. Therefore, the best practice is to validate any intended analytical method from the commercial laboratories before its application for monitoring purposes.

The various nitrosamines found in PCC exhibit a wide range of physico-chemical properties. This means it is highly unlikely that a single monitoring method can adequately capture all of the compounds of interest.

Since volatility was identified as one of the main parameters impacting the sampling and measuring methods, in this guide only volatile nitrosamines with vapour pressures ranging 0.001 – 0.4 kPa are considered.

However, in principle, this guidance is potentially useful for amines within the same range of volatilities (0.001 – 0.4 kPa). Also, it could be potentially useful even for some nitrosamines and amines with lower volatility, but in both cases further research is required and the generating the corresponding validation data will be needed.

5 Periodic monitoring methods

5.1 Available manual methods for volatile nitrosamines (0.001 – 0.4 kPa)

- Method A – Non-isokinetic sampling with dynamic dilution following requirements of CEN TS 13649: 2014 [11]. Adsorption onto appropriate tubes. Amines only, potential application to some nitrosamines but need to be validated. No previously tested in the presence of high humidity (as in the case of PCC stacks).
- Method B – Non-isokinetic sampling with dynamic dilution following requirements of CEN TS 13649: 2014 [11]. Adsorption onto ThermoSorb N cartridges – volatile nitrosamines (potentially amines but need to be validated). Only tested for air quality sampling, not yet for stack sampling. High humidity featuring the PCC stacks is foreseen to be the main limitation.
- Method C - Isokinetic sampling and liquid impingement into 0.1M Sulfamic acid (nitrosamines), 0.1M HCl or 0.05 M H2SO4 (amines) - based on VDI 2467 part 2 [12] or BS EN ISO 21877: 2019 [13]. This method has validation data for 8 nitrosamines under simulated PCC stack conditions [16, 18]. The monitoring requirements are specified in Annex 1, and the method is fully described in Annex 2.

Sample duration: 4 - 6 hours

Storage: Samples must be stored below 6°C during storage and transit to the analytical laboratory. Samples for Method B must be analysed within a week.

Available Analytical Techniques:
- Method A: GC-MS
- Method B: GC-MS
- Method C: GC – TEA (used for the above mentioned validation test, ref. 16 and 18)

Typical analytical Expanded Uncertainty at 95% confidence interval:
- Method A: Dependant on species analysed
- Method B: 10% - for nitrosamines (only lab analytical method)
- Method C: 10% - for nitrosamines (only lab analytical method)
- Method C: Standard deviation of validation data (6):
    - 0.012 to 0.4 kPa: 12% (recovery ≈100%)
    - 0.005 to 0.006 kPa: 20% (recovery 75-80%)

Typical sampling Limit of Detection (LOD):
- Method A: Dependent on dilution ratio
- Method B: Dependent on dilution ratio
- Method C: 0.2µg/m^3 - for nitrosamines with vapour pressures within 0.005 to 0.4 kPa

Limitations:
- Due to the lack of enough validation data for these methods (the field trials on a pilot plant did not produce enough results above the LOD) a typical method uncertainty is difficult to be determined without further validation studies. This in turn means that currently any result from any of these methods is subject to a large amount of unquantifiable uncertainty.
- Method B is applicable to volatile nitrosamines with a vapour pressure higher than 0.002 kPa. Potentially, it can be used for nitrosamines with lower volatilities but may result in reduced capture efficiency, so further testing and validation will be required.
- Typically, in manual extractive testing the absorption efficiency of the first absorber (or first two, when three are in line) of the sampling system is at least 95 % of the concentration of the compound being measured. During laboratory trials of Method B [16, 18], the results of which have been used to develop this guide, total absorber efficiencies for NDMA, NMEA, NDEA, NPIP & NDPA were found to be close to 100%, however only 75-80% for NDBA, NPYR & NMOR (which are less volatile nitrosamines). This would indicate that Method B is more suitable for high or intermediate volatile nitrosamines, but further research is still required into different sampling configurations (e.g., inclusion of a condenser before the impingers, as suggested in section 8 of WP1 report [17]), which may improve absorption efficiency.

- Method A and B are non-isokinetic methods and therefore the sample will not be representative of an in-homogeneous gas matrix.
- Dynamic dilution may not be suitable for gas matrices containing droplets - saturation of the dilution head may occur resulting in sample loss.
- The Method C UK non-accredited analysis technique has been developed and validated for water nitrosamine samples. It requires a volume of at least 1 litre of sample which means that PPC stack samples have to be diluted with water in order to reach the required minimum solution volume. This dilution of the sample may increase the uncertainty of the analysis.

Currently, there are no accredited laboratories in the UK able to carry out the analysis for all of the target species for all of the methods.

5.2 Available instrumental monitoring methods - not specific for volatile nitrosamines

- Method A: FTIR analyser to CEN TS 17337:2019.

The gas should be extracted isokinetically when droplets are present in the stack gas.

Limitations:

- FTIR spectral resolution could prevent the distinction of the target species due to the (likely) overlapping of the nitrosamine and amine species potentially present in the samples. It is worth noting that 21 nitrosamines and 125 amines species have been observed in PCC plants (MetCCUS Task 2.1.1 report, section 5), representing an important source of potential interferences
- FTIR instruments may not have a low enough LOD to provide a quantitative result
- The sampling system and FTIR cell must be heated (usually to 180°C) to prevent condensation and sample loss. This may induce further breakdown of the amine-based solvent within the sampling system, therefore biasing the result

Currently no suitable validated methods are available for automated measuring system – AMS (also called instrumental continuous emission monitor – CEM). Here we mention some analytical instrumental methods which has been used in experimental research. It is worth noting that using any of those with monitoring purposes requires previous testing and the generation of validation data, both for the specific list of target species to be measured and for PCC stack conditions (which are unique and not like standard stack emissions monitoring).

Proton Transfer Reaction Time Of Flight mass spectroscopy (PTR-TOF-MS) and Selected Ion Flow Mass Spectroscopy (SIFT-MS) are relatively new analytical approaches with LODs and accuracy that would be suitable for nitrosamine monitoring. Although these types of instruments have been used for studies on PCC emissions, they have not been typically used in the past for stack emissions and are currently very costly. Furthermore, no testing and validation data has been found in the literature for the application of these techniques to PCC stack monitoring. In the case of mass spectrometers (as SIFT-MS) there is a potential limitation due to the overlapping of several target compounds (amines, nitrosamines, etc.) having the same molecular mass. In principle, instruments having Time Of Flight detectors could be resilient to this mass interference, although the corresponding checks should be made.

6 Continuous emission monitoring systems

6.1 AMS (CEMS) selection

The best practice is to select the AMS (CEMS) systems according to the usual permitting requirements of the process with regards to certifications in place to the appropriate certified ranges.

Care must also be taken to ensure that the system is capable of handling saturated gas streams containing droplets. In-situ cross stack and in stack CEMS may not be suitable, due to the presence of droplets. Extractive systems should be installed with a heated sampling probe to ensure no loss of sample, especially for reactive species such as nitrosamines (and HCl, NH_3 and SO_2 as well)

Special consideration should also be given to the representative sampling of reactive species that could potentially be dissolved in entrained droplets (as amines and nitrosamines).

Most extractive CEMS sampling systems draw sample gas at a fixed rate and are designed to sample a homogenous gas. Sampling an aerosol at a fixed rate, unrelated to the stack gas velocity, will result in a non-representative sample being extracted. Consideration should be given to the isokinetic extraction of the CEMS sample gas. Currently, there is no commercially available solution specifically designed for this purpose. There are, however, automatic iso-kinetic samplers from several manufacturers, designed for the long-term sampling of dioxins or biogenic carbon. These systems could be adapted to incorporate a 'side-stream' connection for the CEMS sampling system into the main iso-kinetic sample stream. Efforts should be devoted to the corresponding testing and validation before using this option for PCC stack monitoring purposes.

6.2 CEMS validation / calibration

CEMS systems should be validated according to the permitting requirements of the process (BS EN 14181:2014 [15] for large combustion plant or waste incinerators).

For reactive species such as HCl, NH_3 and SO_2, a CEMS that is extracting sample from a fixed point at a fixed rate is unlikely to be representative. For these species, the calibration should be carried out using the appropriate standard reference method and carrying out parallel measurement against the CEMS using multipoint isokinetic sampling. Since volatile nitrosamines are also reactive species, the same guidance is encouraged, noting that the corresponding testing and validation should be undertaken separately independently of the analytical technique used to detect and quantify the target compounds.

7 Future work proposals

PCC emissions are a new area within stack emission monitoring, with complexities arising from the requirement to sample "new" species (e.g. amines and nitrosamines), that have not been typically monitored or regulated in the past. There is an added challenge in that these emissions are found within non-typical flue gas characteristics. Although research into new methods and validation of existing methods is being carried out (such work has formed the basis of this guide) further work is still required to enable the industry to meet the challenges posed by PCC stack emissions.

We identify below some key areas for future work:

- Development analytical capability for the list of PCC nitrosamines and amines: Currently analysis options are limited for these species. Analytical methods are not specific to stack samples (matrices) or are not available at the appropriate limit of detection, neither for all the relevant species.
- Investigation into the significance of thermal degradation of amines and nitrosamines in heated sample systems: This affects both periodic monitoring techniques and the selection of CEMS.
- Investigation into different sampling configurations for manual extractive techniques: Different sampling configurations may improve absorption efficiency within the sampling system for some amines/nitrosamines.
- More investigation is required into the effects of particulates and aerosols on PCC emissions.
- Validation of the methods listed in this guide in accordance with the requirements of CEN TC 264.
- Sampling and analysis methods prepared for future standardisation under ISO TC 146 or CEN TC 264.
- Expansion of NPL current test bench capability in the UK to allow more comprehensive laboratory and validation testing for breakdown products (including specific tests for species having different ranges of volatility).

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ANNEX 1. Deliverable 3.

REQUIREMENTS FOR POLLUTANTS AND CO_2 EMISSIONS MONITORING IN AMINE BASED POST COMBUSTION CO_2 CAPTURE.

Authors: H. Barros, R. Harvey, C. Dimopoulos, R. Robinson (NPL).

Lead participant: **NPL**
Other participants: FORCE

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1	NPL National Physical Laboratory	Hampton Rd, Teddington TW11 0LW. London. UK.
2	FORCE TECHNOLOGY	Park Allé 345, 2605 Brøndby DK

Summary

This report forms a part of the project EURAMET / MET CCUS (NPL Report 3917), and is addressing the activity 2.1, Task 2.1.1.

Both the solvent amines used in the Carbon Capture Usage and Storage (CCUS) plants, and their degradation products (secondary amines, nitrosamines, and nitramines) exhibit a complex physicochemical behaviour under the typical Post-Combustion CO_2 Capture (PCC) conditions. This makes it necessary to establish a specific set of requirements for sampling and monitoring of these and other pollutants produced at PCC plants.

This report on requirements for amine-based PCC stack emissions monitoring is meant to provide guidance to regulatory bodies, monitoring contractors, industry and other parties interested in stack emission monitoring associated to CCUS. Also, it contains a survey in the emissions levels reported in the literature for amines and nitrosamines in PCC.

The scope of this report is contributing with additional and specific information to the existing standards and regulations considering requirements for sampling, measurements and monitoring applicable to amine-based PCC plants. It focuses on the emerging pollutants found in pilot plants and laboratory scale studies. When using amine-based PCC, the CO_2 scrubber is composed by one or several amines in an aqueous solution, and the above-mentioned pollutants are mainly breakthrough products resultant from the used amine(s) chemical and thermal degradation during the carbon dioxide capture process. Amongst them it can be found amines, nitrosamines, and nitramines, while this report is focused on amines and nitrosamines given the toxicity and carcinogenicity of many of the species belonging to these two groups of organic chemical compounds.

Throughout this document, guidance to amines/nitrosamines sampling from stacks should be interpreted as also meaning sampling from vents, ducts, and flues, unless otherwise stated.

Finaly, general monitoring requirements of the post-capture flue gas, also called CO_2 depleted flue gas, are also briefly summarised.

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1. Reference to the BS EN 15259 – Measurement of stationary source emissions. Requirements for measurement sections and sites and for the measurement objective plan and report

The Comité Européen de Normalisation (CEN) standard BS EN 15259 is a European standard that is of importance to plant designers, operators, stack emission monitoring organisations, and regulatory bodies.

In summary the BS EN 15259 is focused on the following aspects:
- specifies requirements for stack emission monitoring measurement locations
- applies to both periodic measurements and to continuous emission measurement systems
- outlines the sampling strategy required to obtain a representative sample

This report expands on the requirements of the BS EN 15259 to cover specifically the sampling and monitoring of amines and nitrosamines potentially being emitted to the atmosphere by PCC plants.

The report is not intended as a substitute for the BS EN 15259, instead it refers to the relevant sections of the mentioned standard and is to be used as a complement of that, specifically for the sampling and monitoring of amines and nitrosamines in PCC plants using solvent amines as carbon dioxide scrubber. It is therefore strongly recommended that the reader has a copy of BS EN 15259 and use it as a guidance.

All the relevant concepts and the technical vocabulary found in the BS EN 15259 are used in the report. All the requirements included in the BS EN 15259 standard are assumed to be known by the reader of this report. Amongst these concepts/definitions and their corresponding requirements, it is worth mentioning the following:

1. Periodic and continuous measurements
2. Representative measurement location
3. Principles of representative sampling
4. Periodic sampling using grid measurements
5. Representative sampling of gases
6. Sampling facilities for stack-emission monitoring
7. Risk-management approach to site work

All the above-mentioned definitions, and in general the whole content of the BS EN 15259, is essential for understanding the specific requirements and indications presented in this report.

2 General conditions, features, and processes defining specific requirements for sampling amines/nitrosamines in PCC plant's stacks.

The features of the PCC plants, the processes occurring within these, and the variety and complexity of the amines and nitrosamines targeted during the stack emissions monitoring, make it complex to undertake a proper sampling for those pollutants. A comprehensive summary on this topic was presented in previous reports [NPL 2022 and 2023]. These features justify the application of specific methods and measurements when sampling amines/nitrosamines.

The following situations, processes and conditions have been observed in amine-based PCC, and they can be used as a summary to get insight of the requirements:
- The flue gas has a temperature ranging between 40 and 80 °C, so water can coexist in liquid and gas phases. In the PCC process the temperature of the flue gas is relatively low (to maximize the CO_2 absorption) [Meekoch & Maneeintr, 2020], producing water saturation as a secondary undesired result. Due to this, for both manual and instrumental methods, isokinetic sampling is required to obtain representative samples.
- Presence of solid particulates in the flue gas, as those expected in plants burning coal, fuel oil, biogas, and other fossil fuels, and in kiln industries. These particles are mainly composed by soot, salts, or sulfuric compounds as H_2SO_4. Gas turbines are expected to produce far lower amount of particles, however it is advisable to measure the particles even in this case, since fine and ultra fine particles will trigger the water and amines/nitrosamine

condensation/coagulation in the interface between the liquid-solvent and the air, being this process one of the most important factors enhancing the emissions of amines/nitrosamines up to a factor of two orders of magnitude [Khakharia et al., 2013, 2015 and 2016; Lombardo et al., 2017; Yi et al., 2021].
- Presence of droplets or liquid particles in the flue gas, as those caused by entrainment, condensation of vapourised water, ammonia, HCl, or droplets produced by water condensation/coagulation onto fine and ultra fine solid or liquid particles.
- The amine/nitrosamine have a large range of solubilities, volatilities, and chemical affinities, for that reason it is expected that these compounds are transported as multiphase pollutants, being present in the gas phase, in the droplets, and even sticked to solid particles (if present).
- Some amines and nitrosamines could react in contact of material surfaces (some metals, rubbers, plastics, etc.), then only inert materials as stainless steel, borosilicate or glass should be used to sample these pollutants.
- The monitoring of amines and nitrosamines requires the stack's gas velocity measurements since it is necessary to report the mass emissions.
- The heterogeneity of the flue gas carrying particles/droplets makes it necessary to determine a representative sample location for Continuous Emissions Monitoring. Once determined this specific location, it is advisable to verify its representativity during the periodic wet chemical (manual) sampling champaigns.
- Several factors affect the rate of breakdown of the amine-based solvent (solvent ageing, NOx levels, metal particles from corrosion, sulphur compounds, O_2 levels in the stack gas and temperature).
- The degradation observed at 18 PCC pilot plants and 29 individual campaigns showed that the degree of the amine's degradation (or reciprocally the solvent stability) changes with several operational parameters, being the total liquid-phase heat stable salt concentration and the gas phase ammonia concentration the most useful to obtain information of the degradation of the solvent [Buvik et al., 2021].
- In the PCC process ammonia (NH_3) is the most dominant degradation gas product in the flue gas [Spietz et al., 2018]. On the other hand, the general composition of a PCC's exhaust is also featured by a mix of compounds originated from the flue gas passing through the capture plant, as sulphur dioxide (SO_2), oxides of nitrogen (NOx), carbon dioxide (CO_2), oxygen (O_2), nitrogen (N_2), and water as vapour and droplets (H_2O).

In summary, amongst the compounds observed in the stacks from amine-based PCC plants, there can be found the following ones:

1. Water / humidity (vapour and/or droplets)
2. Oxygen
3. Ammonia
4. Carbon dioxide (CO2)
5. Sulphate and sulphur dioxide
6. NOx
7. Chloride and HCl
8. Formaldehyde and acetaldehyde
9. Heat stable salt/organic acids (nitrite, nitrate, sulphate, acetate, formate, glycolate, oxalate, and propionate have been observed in PCC plants)

All these compounds should be monitored in accordance with the regulations in force and the relevant standard methods. It is worth noting that the emitted CO_2, SO_2 and HCl are the remanent emissions after scrubbing the inlet gas, and they are present in much lower concentrations. However, it is important to monitor the remining CO_2, since the direct measurements significantly reduce the uncertainties of simple estimations based on mass balance.

The CO_2 capture efficiency in PCC plants depends on several parameters, and it has been observed to be variable. Also, estimations of the emitted CO_2 based on mass balance has larger uncertainty in comparison with a direct measurement. For all the above reasons, CO_2 should be monitored in accordance with the regulations in force and the relevant standard methods.

3 Sampling requirements for amines/nitrosamines in PCC stacks by wet chemical sampling (manual sampling)

Although there is experience on the typical emissions from large combustion plants, there is a considerable knowledge gap associated with the specific PCC's pollutant emissions (such as amines and nitrosamines) and their typical concentrations. It has been shown that within systematic experiments, nitrosamine formation yield is proportional to the concentration of common secondary amines generated by MEA degradation (such as HeGly, HEEDA and DEA) and it is a function of CO_2 loading and temperature [Fine *et al.,* 2014; Meekoch & Maneeintr, 2020]. It is then advisable to monitor secondary amines on atmospheric emissions, along with the main amine(s) used in the solvent itself and the nitrosamines.

Specific requirements for amine-based PCC amines/nitrosamines stack monitoring using wet chemical methods (manual methods) includes the following:

1. Grid measurements sampling
2. Isokinetic sampling
3. Monitoring particles (reported as #/m^3 @ 1 atm and 0 ºC)
4. Monitoring droplets (reported as #/m^3 @ 1 atm and 0 ºC)
5. Impinger train and used chemicals
6. Sampling handling, preservation and transporting
7. Certified laboratory analytical methods

There are no available standard methods for manual sampling and monitoring of amines and nitrosamines. However, the relevant physicochemical parameters of those two groups of compounds covers similar ranges, in fact they differ only in the presence of the amino chemical group (amines) or the nitroso chemical group (nitrosamines), but apart from that, they essentially are constituted by the same organic chains [NPL 2023]. This implies that both kind of chemical compounds requires similar sampling systems and methods. In the literature there can be found several application cases of wet chemical impinger sampling for nitrosamines, and a summary was presented in a previous report [NPL 2023], which includes the only available performance assessment and validation of the sampling method (up to our knowledge).

Regarding the requirements 5, 6 and 7 on the previous list, NPL recently produced two separated reports, *Guidance for the Measurement of Emissions from Post Combustion Carbon Capture Processes* [NPL 2024 (a)] and *Stationary source emissions — Determination of mass concentration of volatile nitrosamines from installations implementing carbon capture systems — Absorber-based method* [NPL 2024 (b)]. In the above-mentioned documents, it is specified that sulfamic acid (0.1 M) is used to prevent undesirable nitrosamine formation during sample storage. Now it is worth noting that this is done by avoiding the interaction between nitrites and the secondary amines, which will be also preserved by the same mechanism. For that reason, amines and nitrosamines are both preserved using this chemical compound, and the sampling preservation, storage and handling will be the same for both (details indicated in the previous reports quoted above).

There is a large number of amine and nitrosamine species potentially emitted in PCC plants, and their presence/absence is related to the used solvent (typically a diluted single amine or amine mixture) and to several plant features and working operation conditions. There is no fix or general-purpose list of amines/nitrosamines to be monitored, so it is necessary to apply a screening method (chromatography / spectroscopic) to identify the compounds present in the flue gas, to then proceed with the quantification, held together with a literature study on the potential degradation products and possibly comparison with degradation product reported in other studies. Certified laboratories with validated analytical methods for the amines and nitrosamines of interest are required for the determination of the concentration of those chemicals within the obtained samples.

4 Sampling requirements for amines/nitrosamines in PCC stacks by continuous emissions monitoring systems.

Specific requirements for amine-based PCC amines/nitrosamines stack monitoring using continuous monitoring methods (instrumental methods) includes the following:

1. Representative measurement location.
2. Isokinetic sampling.

There are no standard methods available for continuous monitoring of amines and/or nitrosamines in PCC stacks. However, several techniques have been proposed and experimentally employed in PCC pilot plants in the frame of research projects in several countries, having obtained a variety of results [NPL 2023]. In general, the main used instrumentation includes:

- FTIR: Fourier Transform Infrared Spectroscopy
- PTR-MS: Proton Transfer Reaction Mass Spectroscopy

In principle, these methods could measure the species of interest. However, it will be challenging to detect and measure the large number of species (amines and nitrosamines) that could be present simultaneously in the stack emissions due to vast range of properties featuring the species found in PCC and the vast variety of their behaviours. For instance, the range of volatilities for nitrosamines expands over 7 orders of magnitude and for 9 orders of magnitude for amines, including from highly volatile compounds to oily and sticky materials hardly volatilised. These may require different temperatures for their injection into the measurement system, but the sampling temperature (the heating lines) should be kept as low as necessary to prevent any compound decomposition during the sampling, making this trade off something worth to study.

On the other hand, many amines and nitrosamines have similar structures, masses, and polarities, and this could compromise the resolution of the spectroscopic techniques. The potential limitations in the spectral resolution are more relevant in the case of FTIR, due to the non-discrete features of the IR spectra. PTR-MS is a promising method to be applied in PCC stacks for amines and nitrosamines, although high mass resolution PTR-TOF-MS is required for several relevant nitrosamines (see discussion below). Finally, validation data is still required before any standard method is developed, regardless the analytical method applied. Some examples of mass interferences follow, this does not pretend to be an extensive or complete list, rather than some iconic cases.

Two of the most volatile nitrosamines found in PCC plants are NDMA and NMEA, both are degradation products of MEA and/or other solvent amines as DMA, DMELA and DEELA [Chen et al., 2018]. However, NDMA could interfere with propionic acid, another MEA degradation product [Chahen et al., 2016] having the same molecular mass (74 g/mol) and the same vapour pressure (0.4 kPa @ approx. 25 ºC). The difference in mass of these two species is about 0.0105 g/mol, requiring a resolution of about 7050. In general, the PTR-TOF-MS resolutions are between 5000 and 10000, so in this case a modern high-resolution equipment is required to measured NDMA without the propionic acid interference.

For its part, NMEA could interfere with n-butyric acid [Strazisar et al., 2003], since both are MEA degradation products having the same molecular mass (88 g/mol) and a vapour pressure in the same range (0.2 to 0.5 kPa @ 25 ºC). In this case, the mass difference is about 0.0112 g/mol, so the required resolution is even higher, about 7790. This can be achieved only with the most advanced PTR-TOF-MS. Also, in the case of using not only MEA but other solvent amines mixes, these nitrosamines could interfere with PDA, DMEN, DMEDA or other solvent amines [SCOPE 2023; Lepaumier et al., 2009].

It is well known that for compounds with vapour pressures below 0.01 kPa (@ 25 °C) the direct use of PTR-MS has low sensitivity, unless the lines are heated. The used measurement system should be able to continuously operate at hight temperature. Even in that case the measurement of semi-volatile or low volatility compounds require specialised setups to minimize surface interactions and improve response times, e.g., some authors has highly improved sensitivity and a special inlet design, reducing wall losses for low volatility compounds compared to standard PTR-TOF instruments [Fischer et al., 2021]. It is necessary in the present context since several nitrosamines (and amines) found in PCC plants shall be regarded as semi-volatile or even low volatile “sticky” compounds, due to its vapour pressure values, and they can be readily adsorbed or condensed onto surfaces.

For instance, some authors have measured low volatility compounds like Cis-pinonic acid (CAS 61826-55-9, VP ≈ 1.3 10^{-7} kPa) or Levoglucosan (CAS 498-07-7, VP ≈ 2.4 10^{-8} kPa) using a PTR-MS system with a heated inlet at 200 ºC, finding that the corresponding instrumental response times (to have only $1/e^2 \approx 13.5\%$ of the signal) for these sticky / low-volatility compounds were in the order of one and 6 minutes respectively [Mikoviny et al., 2010]. A similar situation is likely to occur for nitrosamines as DNPZ (VP ≈ 4.3 10^{-7} kPa) or NHeGly (VP in the order of 8 10^{-8} kPa), and also for the other four PCC nitrosamines with even lower volatility (NDBzA, NDiNA, 4-Nitroso-1-piperazineethanol and 1-nitro-4-nitrosopiperazine). These nitrosamines could be present in the PCC stack emissions due to its solubility (they are transported by the mist), and these could be challenging the near real-time measurements.

In the case of low volatile nitrosamines, also several mass interferences appear. For instance, NHeGly, Mea Urea, BHEEDA and the secondary amine N,N'Bis(2-hydroxyethyl)ethylenediamine, are all produced by MEA degradation [Akram et al., 2022, Chahen et al. 2016; Lepaumier et al. 2009] and all of them have the same molecular mass (158 g/mol) and similar vapour pressure (all approx. 10^{-7} kPa). It is evident that the larger the molecular mass the higher the required resolution (which is a relative value).

Another aspect that requires more research is the potential fractionation of the amines, nitrosamines and other VOCs found in PCC when analysed by PTR-MS. The large number of compounds and their diversity make it difficult to foreseen which are going to be the potential mass interferences in situations where heavy molecule fractions could interfere with smaller molecules preserving their structure during the protonation.

In Section 5 there is a comprehensive list of amines and nitrosamines found in PPC plants and laboratory scale facilities simulating industrial conditions.

Although all the aspects mentioned in the previous paragraphs, several compounds can be measured simultaneously [Buvik et al., 2021]. However, it is worth noting that regardless the method selected for continuous sampling and monitoring of amines/nitrosamines, during the method development it is required the corresponding testing and validation against wet chemical (manual sampling) methods.

Again, certified laboratories with validated analytical methods for the specific amines and nitrosamines are required for the determination of the concentration of those chemicals within the obtained samples.

5 List of amines and nitrosamines found in PCC pilot plants and laboratory scale testing facilities.

A large number of amines and nitrosamines are produced and potentially emitted from amine-based PCC plants. In each case, the specific list of amines and nitrosamines depends on the solvent composition, plant design, operational parameters, inlet flue gas composition, corrosion of the plant, aging of the solvent and control measures in place [NPL 2023; SCOPE 2023; Vevelstad et al. 2022; Buvik et al. 2021; Saeed et al 2018; Vega et al. 2016; Voice et al. 2013; Lepaumier et al. 2009]. That is why it is important to identify which specific species are being produced in each place and to quantify them. However, it is challenging to sample and measure all the relevant compounds actually present in the CO_2 depleted flue gas (off gas).

No list of amines and nitrosamines of concern in PCC has been agreed by the scientific community and the regulatory bodies. Table 1 summarises 125 amines observed in PCC pilot plants and/or laboratory scale facilities, using MEA and other popular solvents (as PZ). These have been measured in emissions, condensates, or solvent solutions, meaning that they are susceptible to be emitted to the atmosphere. This list includes references from 2003 to 2023, more than 140 documents were consulted (papers, reports, PhD thesis, conference proceedings, etc.), and the information in the Tables resulted from 65 of them. A further update is necessary since this is a fruitful area of research. Additional species mentioned only in theoretical, or modelling studies were not mentioned in this report (this applies to the entire report).

Table 1. Amines observed at PCC plants and lab scale test facilities.

Amines		Amines		Amines	
CAS	Acronym.	CAS	Acronym.	CAS	Acronym.
100-37-8	DEELA / DEEA	141-43-5	MEA	536-78-7	3-ethylpyridine
100-71-0	2-ethylpyridine	142-25-6	3MEDA*	5422-34-4	N-(2-hydroxyethyl)-lanthamide
10111-08-7	2-imidazole-carboxaldehyde	142-26-7	HEA	5625-67-2	2-PO
102-71-6	TELA / TEA	142-84-7	DPA	56-40-6	Glyc / GLY
103-76-4	PZE / HEP	144236-39-5	HEHEAA	5835-28-9	HEGLy
104-90-5	5-ethyl-2-methylpyridine	14667-55-1	2,3,5-TM-pyrazine	583-61-9	2,3-dimethylpyridine
105-59-9	MDEA	150-25-4	Bicine	59702-23-7	1HEPO
105-84-0	1,4,7-Trimethyl-diethylenetriamine	15438-70-7	MEA urea / BHEU	60-35-5	Acetamide
106-58-1	DMP	156-87-6	PLA / AP / 3AP	60487-26-5	2-[2-[bis(2-hydroxyethyl)amino] ethylamino]ethanol
107-10-8	PA / MPA	1615-14-1	HEI	61877-80-3	N,N,N'-Trimethyl-N'-[2-(methylamino)ethyl]-1,2-ethanediamine
107-15-3	EDA	1615-15-2	HEMI	624-78-2	EMA
108-00-9	DMEN	16250-70-7	2-Methyloxazolidine	6719-02-4	HEPyr
108-01-0	DMEA / DMAE	16250-71-8	2-Ethyloxazolidine	68-12-2	DMF
108-99-6	3-Mpy	17026-89-0	2-ethyl-2-methyloxazolidine	693-06-1	HEF
109-01-3	1MPZ	17225-70-6	2-(Methyl(2-(methylamino)ethyl) amino)ethanol	694-32-6	1-Methyl-2-imidazolidinone
109-06-8	2-Mpy	18190-44-8	HESucc	71298-49-2	1,3-Bis(2-hydroxyethyl)imidazolidin-2-one
109-07-9	2MPZ	1871-89-2	BHEOX	74-89-5	MA / MMA
109-08-0	2-MP	19836-78-3	3-Methyl-2-Oxazolidinone	75-04-7	EA
109-81-9	2-Methylamino-ethylamine	236-416-6	2-ethyl-5-methylpyrazine	75-12-7	FA
109-83-1	MMA / MAE	23936-04-1	4HEPO	75-50-3	TMA
109-89-7	DiEA	23936-14-3	2,5-BHEPDO	7663-77-6	APP
109-97-7	Pyrrole	2403-88-5	DMPD	7755-92-2	1FP / FPZ
110-18-9	TMEDA	25209-64-7	1-formyl-4-(2-hydroxyethyl) piperazine	77-86-1	TRIS
110-70-3	DMEDA	26654-39-7	4-Dimethyl-2-oxazolidon	80-73-9	DMEU
110-73-6	EAE	2761991-15-3	1-(1-Hydroxy-2-methylpropan-2-yl)-4,4-dimethylim idazolidin-2-one	Next 3 CAS No.	DM-Pyrazine, DM
110-85-0	PIP / PZ	27646-80-6	MeAMP	123-32-0	2,5,DM
110-91-8	MOR	280-57-9	TEDA	108-50-9	2,6,DM
111-41-1	HEEDA / AEEA	290-37-9	Pyrazine	5910-89-4	2,3,DM
111-42-2	DEA	3030-47-5	PMDTA	Next 3 CAS No.	2EMP
1120-64-5	2-Methyloxazoline	3197-06-6	BHEEDA	13925-03-6	2,6,EMP
112-57-2	TEPA	3356-88-5	HEOD	236-416-6	2,5,EMP

115-69-5	AMPD	3512-80-9	2,6-dimethyl-4-pyridinamine	15707-23-0	2,3,EMP
120-93-4	2-Imid	3586-25-2	HHEA	PubChem CID 129880212	2-hydroxyethylamino-N-hydroxyethyl-acetamide
121-44-8	TEA	36731-41-6	2-ethyl-6-methylpyrazine	PubChem CID 13449561	1,4-Dimethylpiperazin-2-one
122-96-3	BHEP	3699-54-5	HEIA	PubChem CID 162441368	2-[2-Hydroxyethyl(2-piperazin-1-ylethyl)amino]ethanol
124-40-3	DMA	4439-20-7	N,N'Bis(2-hydroxyethyl) ethylenediamine	PubChem CID 17881670	1-[2-(Dimethylamino)ethyl]-2-imidazoldinone
124-68-5	AMP	497-25-6	OZD	PubChem CID 22152606	1,3,4-Trimethylpiperazin-2-one
13750-81-7	1-methyl-2-imidazolecarboxaldehyde	504-76-7	Oxazolidine	PubChem CID: 22949116	3,4,4-trimethyl-1,3-oxazolidin-2-one
13925-00-3	2-Ethylpyrazine	504-77-8	2-oxazoline	PubChen CID 43498335	AEHEIA / HEAEIA
139-87-7	EDELA	51200-87-4	DMO	Unknown	1-hydroxyethyl-3-homopiperazine
140-07-8	THEED	53019-51-5	2-propyloxazolidine	Unknown	HEHEPA
140-31-8	AE-PZ / AEP	5308-25-8	EPZ		

Notes: Table 1 is organised by CAS or by PubChem CID number (two unknowns)

Table 2. Other amines used and/or proposed for amine-based PCC.

Amines		Amines		Amines	
CAS	**Acronym.**	**CAS**	**Acronym.**	**CAS**	**Acronym.**
108-16-7	1DMA-2P	13531-52-7	PETA	4620-70-6	TBEA
109-55-7	DMAPA	1484-84-0	2PPE/2-PiperEtOH	6291-84-5	MAPA
109-76-2	PDA	1643-19-2	TBAB	71-44-3	Spermin
110-89-4	Piper/PIP	1696-20-4	AMOR	7328-91-8	DMPDA
110-97-4	DIPA	288-32-4	IMD	78-96-6	MIPA
111-40-0	DETA	2955-88-6	1-(2HE)PRLD	929-06-6	DGA
115-70-8	AEPD	3040-44-6	EtOH-Piper	Tetra-N-methylpropanediyldiamine	TMDPA
124-20-9	Spermid	3179-63-3	DMPA	1-Amino-1-cyclohexylaminopropane	ACHP
13325-10-5	AB	33329-35-0	TMBPA	-	-

Table 2 includes additional species related to amines used and/or proposed for amine-based PCC. This includes only species not mentioned in Table 1. They have been summarised from the literature [SCOPE 2023; Vega et al. 2016; Voice et al. 2013; Lepaumier et al. 2009]. Table 3 lists 21 nitrosamines observed in PCC pilot plants and/or laboratory scale facilities, which have been measured in emissions, condensates, or solvent solutions. Again, this experimental evidence imply that these species are susceptible to be emitted to the atmosphere by PCC plant stacks.

Table 3. Nitrosamines observed at PCC plants or lab scale test benches. Breakdown products of **MEA** */AMP-PZ*

Nitrosamines		Nitrosamines		Nitrosamines	
CAS	**Acronym.**	**CAS**	**Acronym.**	**CAS**	**Acronym.**
100-75-4	**NPIP**	26921-68-6	NMELA	601-77-4	NDIPA
10595-95-6	**NMEA**	39884-53-2	NMOx	621-64-7	NDPA
107938-05-6	1-nitro-4-nitrosopiperazine	48121-20-6	4-Nitroso-1-piperazineethanol	**62-75-9**	**NDMA**
1116-54-7	**NDELA**	5336-53-8	NDBzA	80556-89-4	N-HEGly
1207995-62-7	NDiNA	55-18-5	NDEA	924-16-3	NDBA
13147-25-6	EHEN / NEELA	**5632-47-3**	**MNPZ (NPZ)**	930-55-2	NPYR
140-79-4	DNPIPA / DNPZ	**59-89-2**	**NMOR / NSMO**	997-95-5	NDIBA

6 PCC emissions range of nitrosamines

Table 4 shows the emission levels of nitrosamines reported in the available literature, all of them performed during experimental test in pilot plants. Also, the calculated required Limit of Detection for the lab-based analytical methods for some selected species, or for the total nitrosamines method (TONO), at a number of PCC plants is shown. This calculation was done using the reported nitrosamine emissions levels and assuming that these plants were to be monitored using the same sampling manual method, sampling time, isokinetic flow rate and liquid impinger volumes as the ones used in a field campaign by NPL in 2023 [NPL 2024(b)].

Briefly the manual sampling system included, consecutively, three absorbers with 100ml 0.1M sulfamic acid solution, one absorber (impinger flask) empty, and a last one with 200 g of silica gel. Additional ThermoSorb cartridges were used to verify potential breakthroughs out the sampling system. The method required isokinetic sampling over a period of 5-6 hours per test, where 6-7 Nm^3 of flue gas was extracted per test. The analytical method used was GC-TEA [NPL 2024(b)].

Within these plants described in Table 4, half of those samples would result in undetectable levels of nitrosamines, or close enough to the worst-case uncertainty ranges for them to be considered accurate. This also presumes that the LoD's provided by the laboratories are correct and achievable (but sometimes it depends on matrix effect and/or potential interferences).

Table 4. Reported emission levels of nitrosamines in PCC and calculated analytical LoD required (based on the method used during the NPL campaign in 2023).

PCC Plant	Year	Reported emissions µg/m³	Nitrosamines Acronym	Total sampled µg	Required LoD µg/L
Maasvlakte pilot PCC [da Silva et al., 2013]	2012	0.005 0.047	NDMA, NMOR	0.027 to 0.25	0.023 to 0.21
Tata pilot PCC [NPL 2024(b)]	2023	0.04 0.08	NDMA, NDPA, NMOR	0.22 0.43	0.18* 0.36*
Loy Yang Pilot PCC [Azzi et al., 2014]	2014	0.4	NMOR	2.2	1.8
Gassnova [SEPA, 2015]	2014	0.1	NDEA, NDMA, MNOR	0.54	0.45
Reported PCC stack emissions [SEPA, 2015]	2015	5	TONO	27	23
Mongstad Test Centre [Berglen et al., 2010]	2010	5	NDMA	27	23
Ferrybridge, CCPilot100+ [Fitzgerald et al., 2014]	2014	20	TONO	110	90
		11	NDINA	59	50
		3.1	NDIBA	17	14
		0.5	NDBA	2.7	2.3
		0.2	NDMA	1.1	0.9

Note: Values highlighted with * were measured with a declared LoD of 0.1 µg/L.

Regarding the analytical performance requirements for compliance monitoring, when carrying out monitoring for research purposes, the analysis method selected is generally that with the highest performance – i.e. the lowest LoD and relative measurement uncertainty. On the other hand, when monitoring to demonstrate compliance with an emission limit, the monitoring performance requirements are tailored to the emission limit to ensure that they

are appropriate for the application. - e.g. measurement uncertainty requirements are expressed as a percentage of the emission limit value. This means that the requirements for compliance monitoring may not be the same as those for research.

As an example, the UK MCERTS Performance Standard for Manual Stack Emissions Monitoring Organisations states that the minimum requirement for the sampling field blank should be <10% of the emission limit value (section 6.5.7). In order to demonstrate this, the sampling limit of detection (in mg/m^3) must also be <10% of the emission limit value.

For the purposes of compliance monitoring, the suitability of any chosen laboratory analysis must be assessed against proposed emission limit values. This means that laboratories that might not fulfil the requirements for research, may be appropriate for compliance measurements

Regardless of location, the logistical issues which arise through the shipping of samples from the PCC site to the analytical laboratory can be extremely detrimental to the accuracy of results produced on analysis. Due to the volatile nature of the target species, matrix composition is important to ensure that the potential for further breakdown after sampling is reduced. This can also be further ensured by samples being always kept below < 6 °C, from stack sampling to measuring in the laboratory. However, as was found in the previous phases of this project, maintaining refrigerated samples at the required temperatures can be problematic [NPL 2023].

It is worth noting that there is a concerning gap in the availability of analytical laboratories that could analyse the whole list of species of interest (amines and nitrosamines) already identified in PPC (see Tables 1, 2 and 3). Furthermore, there are laboratories that are well versed with the analysis of nitrosamines and amines within lipid-based samples from the pharmaceutical industry and air quality samples. Unfortunately, this expertise did not translate to the analysis of PCC emerging pollutants, since the list of target species is not the same and neither the matrices, which are aqueous samples from PCC stack emissions sampling (neither to sorbent tubes nor cartridges). Although there are some laboratories with potential for developing specific methods for PCC stack monitoring, this needs a substantial funding to produce viable methods or results.

7 Inapplicability of toxic equivalents for amines and nitrosamines

There are fundamental limitations on the application of Toxic Equivalents for monitoring amines or nitrosamine emissions originated in PCC. The amines are compounds with a functional group that contain a nitrogen atom with a lone pair, so the number and variety of organic amines potentially emitted by PCC involves different compounds and behaviours. The nitrosamines have a nitroso functional group (N-N=O) in otherwise completely different organic compounds. Therefore, there is a wide range of values for all the relevant physical and chemical parameters related to their susceptibility to undergo into specific chemical reactions, or driving their formation, stability, transport, and thermodynamical behaviour. For example, the nitrosamine's vapour pressure covers 7 orders of magnitude, while for amines this range extends 9 orders of magnitude. Also, their solubilities variates among the different species, they include linear compounds and ring type species, and their molecular masses goes from about 30 to 300 g/mol.

The selection of any surrogate substance assumes that the selected species has similar physicochemical properties, transport behaviour, toxicological effects, and/or environmental fate properties as the whole group of compounds pretending to be represented, but none of these assumptions holds in the case of the amines or nitrosamines. For that reason, it is not possible to find a surrogate capable of representing any of the two compound's families. The application of a Toxic Equivalent approach or the use of surrogate species for monitoring purposes is only valid in cases where the target molecules are similar enough regarding their dynamic (transport, dispersion, sampling recovery, etc.), as in the case of dioxins which comprises all the different species within ±14% of the median mass (288 g/mol).

Therefore, in the case of amines and nitrosamines the argument of "similarity" required to define a surrogate cannot be accomplished. The equivalent or surrogate species approach is unrealistic in this case, since any selected species will be not representative of the whole group of amines or nitrosamines found in PCC. For instance, the masses of

the amines and nitrosamines species found in PCC expand from 31 to 322 g/mol and from 74 to 299 g/mol, respectively. For all that, this kind of over-simplified approach should not be used in PCC amine/nitrosamine monitoring.

Also, figures as the EAL proposed by the Norwegian Institute of Public Health (0.3ng/m3) for total nitrosamines expressed as NDMA [Svendsen et. al., 2023], cannot be easily adopted as a fully derived and established benchmark due to the differences in the way that different countries assess carcinogenicity [SEPA, 2015].

8 CO_2 depleted flue gas general monitoring requirements

Regarding the CO_2 depleted flue gas (off gas) composition, some authors have recommended using reference standards employed to monitor compliance with air emissions regulations for high-accuracy depleted CO_2 gas composition measurements [Thimsen et al. 2014].

Instrumental methods (also called continuous emissions monitoring and sampling methods - CEMS) are recommended for most flue gas components. An example is the Fourier Transform Infrared (FTIR) systems which can monitor simultaneously several gases of interest.

Regardless the selection of the instrumental method, the reported CO_2 depleted flue gas composition should be sufficiently accurate and precise to meet the requirements of the standards in use. This should be demonstrated against the procedures in the respective reference methods. The selected instrumental system should be calibrated against primary calibration standards weekly or on a frequency that results in instrument drift of no more than 2% on calibration gases.

Table 5 contains the most relevant flue gas components and the recommended quantification reference methods. Instrumental methods are available for all non-condensable, non-soluble flue gas components. The condensable/soluble flue gas components require extractive sampling reference methods.

Table 5. Requirements for CO_2-depleted flue gas sampling and monitoring.

Component	Reference method	Notes
Oxygen (O_2) Carbon dioxide (CO_2) Carbon monoxide (CO) Sulphur dioxide (SO_2) Nitrogen oxides (NO and NO_2)	EN 14789: 2017 CEN TS 17405: 2020 EN 15058: 2017 CEN TS 17021:2017 EN 14792: 2017	Instrumental methods (CEMS), dried sample from common sampling point
Total HC Water / humidity	EN 12619: 2013 EN 14790: 2017	Instrumental methods (CEMS), Manual extractive
Aldehydes Formaldehyde	CEN TS 13649: 2014 CEN TS 17638	Sorbent capture Manual extractive
Particulates Particulates metals Sulfuric acid (H_2SO_4) Ammonia (NH_3)	EN 13284-1 EN 14385: 2023 CEN TS 17638 EN ISO 21877: 2019	Extractive traverse sampling reference methods
Flow	EN 16911-1 EN 16911-2	Measurement for flow profile and iso kinetic methods Application of 16911-1 to flow CEMs and EN 14181
Temperature and pressure	Nonspecific	Requirements detailed in EN 16911-1 and EN 13284-1

Flue gas sampling ports should be used to sample from the duct near the existing flue gas flow meters, to allow a better comparison of CEMS and manual monitoring results.

In the case of instrumental methods (CEMS), it is required the corresponding testing and validation against wet chemical (manual sampling) methods. The periodicity of these verifications and the wet chemical methods should be in accordance with the current regulations.

9 Other parameters related with the atmospheric emissions

There are several parameters that are generally assessed as long-term process/plant monitoring indicators. These are key performance indices that can only be assessed over many hours of operation and include chronic effects as well as intermittent operations [Thimsen et al. 2014].

The condition/composition of several of these parameters are related to the level of amines degradation products being produced, accumulated (in the scrubber/lean solution) and emitted to the atmosphere. In some cases, these has been also used as indirect indicators of the potential atmospheric emissions of amines and nitrosamines (amongst other pollutants as SO_2, H_2SO_4 or metals), although correlations generally valid has not been found.

It is worth mentioning that the generated information can be used to assess the potential toxicity and impact of the corresponding waste streams (solids and/or liquids including potential leaks), for which appropriate systems of management and final disposal should be in place.

These additional parameters are related with the composition or condition of the items listed below:

- Flue gas source and flow rate
- Material uses
    - Amine solution (scrubber/rich amine & stripper/lean amine) composition
    - Water blowdown
    - Shower waters
- Intermittent waste streams
    - Amine reclaim-waste
    - Lean-solution filter cake
    - Spent activated carbon (filters)
- Heat exchanger fouling/corrosion
- Gas-liquid contactor fouling/corrosion/foaming
- Accumulation/emission of degradation/corrosion products

Some of the main target compounds used to characterise the previous items are the following:

- Particles (in the case of the flue gas source)
- Secondary amines
- Nitrosamines
- Nitrites (NO_3^-)
- Ammonia
- Heat stable salt/organic acids (acetate formate, glycolate, oxalate)
- Metals (from corrosion and fuel)
- Sulphur compounds

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ANNEX 2. Deliverable 3.

Manual stack sampling method for volatile nitrosamines in post combustion CO_2 capture plants.

Authors: H. Barros, R. Harvey, H. Cheales-Norman, C. Dimopoulos, R. Robinson.

Lead participant: **NPL**

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1	NPL National Physical Laboratory	Hampton Rd, Teddington TW11 0LW. London. UK.

Summary

Carbon dioxide capture could contribute significantly to achieve emissions neutrality, reducing existing greenhouse gases inputs from industrial processes and compensating for residual emissions that are hard to eliminate. Among the different carbon capture technologies, amine-based Post-combustion Carbon Capture (PCC) is the most widely used and has the greatest momentum, due to a series of technical and commercial advantages. However, the degradation products of the sorbent amines used in PCC (amines, nitrosamines, etc.) are potentially emitted to the atmosphere, impacting health and environment.

This report forms a part of the project EURAMET / MET CCUS and is addressing the activity 2.1, Task 2.1.2. scoped to propose a candidate method for nitrosamines monitoring in Post Combustion Carbon Capture (PCC) plants. This document proposes a method for monitoring the emissions of nitrosamines from the stacks (exhausts) of PCC, specifically aimed at processes utilizing amine-based solvents as the carbon capture medium.

Table of Contents

1 Introduction

This document proposes a manual sampling method for monitoring volatile nitrosamines from stacks or any others ducted gaseous streams. It is primarily developed for the measurement of emissions from amine-based post combustion CO_2 capture processes.

The method was successfully tested in laboratory trials for a selected group of volatile nitrosamines at around 1 µg/m3 per species under PCC simulated conditions. The tested nitrosamine species have vapour pressures ranging 0.005 – 0.4 kPa, values at atmospheric pressure and 20 ºC (details included in the Task 2.1.4 report). On the other hand, during one field test, concentrations encountered were mostly below the analytical limit of detection. Therefore, the monitoring durations specified in this document are designed to maximise the sample volume obtained.

This method is applicable to volatile nitrosamines with a vapour pressure higher than 0.002 kPa approx. In principle, the method could be used for nitrosamines with lower volatilities than the ones tested here, but it is unknown what is the lowest volatility limit to apply this method (lowest vapour pressure value for which this method is still suitable). Also, attempting the sampling of low volatile compounds with the present method may result in reduced capture efficiency. Since using the present method for compounds with lower volatilities could not be adequate. this should be tested and validated separately. On the other hand, all nitrosamine volatilities are lower than that for the water (vapour pressure 2.3 kPa at 20 ºC). In fact, the highest volatile nitrosamine observed in PCC plants is NDMA, whose vapor pressure is 0.4 kPa, so no upper limit is specified for the application of this method in term of nitrosamine volatility.

The method assumes that the gas is saturated, with droplets, produced by entrainment and/or condensation/coagulation. This implies that the gas flow in the stack (duck) could be heterogeneous and that nitrosamines (generally soluble compounds) can be partially transported by the water droplets. Therefore, sampling shall be carried out isokinetically.

Regarding the analysis of the nitrosamines sampled generated by the proposed method, there is no reference method used to analyse liquid samples for nitrosamines. Either gas or liquid chromatography (GC or LC) is typically used, together with an analytical method (such as FID, Thermal Energy Analysis, Fourier Transform Infrared Spectroscopy, Mass Spectrometry, or Proton Transfer Reaction Mass Spectrometry). It is worth mentioning that most analytical laboratories do not provide measurements for the suit of nitrosamines observed in PCC plants

2 Normative references

The following documents are essential references to the text. Some or all their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document applies (including any amendments).

BS EN 15259:2007, Air quality — Measurement of stationary source emissions — Requirements for measurement sections and sites and for the measurement objective, plan, and report

BS EN 13284-1:2017, Stationary source emissions — Determination of low range mass concentration of dust.

BS EN ISO 16911-1:2013, Stationary source emissions — Manual and automatic determination of velocity and volume flow rate in ducts.

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

Absorber
a device in which specific elements are absorbed into an absorption liquid. [EN 14385:2004, 3.1]

Absorber efficiency
ratio of quantity of an individual nitrosamine collected in the first two absorbers divided by the quantity of the individual nitrosamine in the first, second and third absorber. [BS EN 14791:2017, 3.18]

Capture efficiency
efficiency of the method to capture the total concentration of the targeted nitrosamine(s) within the flue gas.

Emission limit value ELV
limit value given in regulations such as EU Directives, ordinances, administrative regulations, permits, licences, authorisations, or consents. ELV can be stated as concentration limits expressed as half-hourly, hourly, and daily averaged values, or mass flow limits expressed as hourly, daily, weekly, monthly, or annually aggregated values. [BS EN 15267-4:2017, 3.37]

Field blank
test sample obtained according to the field blank procedure [BS EN 14791:2017, 3.29]

Field blank procedure
Procedure used to ensure that no significant contamination has occurred during all the steps of the measurement. This includes for instance the equipment preparation in laboratory, its transport and installation in the field as well as the subsequent analytical work in the laboratory. [BS EN 14791:2017, 3.30]

Field blank value
Result of a measurement performed according to the field blank procedure at the plant site and in the laboratory [BS EN 14791:2017, 3.31]

Isokinetic sampling
Sampling at a flow rate such that the velocity (v_n) and direction of the gas entering the sampling nozzle are the same as the velocity (v_d) and direction of the gas in the duct at the measurement point [BS EN 13284-1:2017, 3.5]

Analytical limit of detection
Lowest amount that the analytical laboratory can detect of the selected species.

Measurement line
Line in the measurement plane along which the measurement points are located, bounded by the inner duct wall [BS EN 15259:2007, 3.15]

Measurement plane
Plane normal to the centreline of the duct at the sampling position. The measurement plane is also known as sampling plane [BS EN 15259:2007, 3.13]

Measurement point
Position in the measurement plane at which the sample stream is extracted, or the measurement data are obtained directly. The measurement point is also known as sampling point [BS EN 15259:2007, 3.16]

Measurement port
Opening in the waste gas duct along the measurement line, through which access to the waste gas is gained. Measurement port is also known as sampling port or access port [BS EN 15259:2007, 3.18]

Measurement method
Method described in a written procedure containing all the means and procedures required to sample and analyse, namely field of application, principle and/or reactions, definitions, equipment, procedures, presentation of results, other requirements, and measurement report [BS EN 14793:2017, 3.4]

Measuring system
Set of one or more measuring instruments and often other devices, including any reagent and supply, assembled and adapted to give information used to generate measured quantity values within specified intervals for quantities of specified kinds [JCGM 200:2012, 3.2]

Measurement
Set of operations having the object of determining a value of a quantity. The operations can be performed automatically.

Individual measurement
Measurement carried out over a defined period of time. Information on the start and end time of the measurement can be of importance, e.g., in case of parallel measurements of the reference method with an automated measuring system to be calibrated or validated [BS EN 15259:2007, 3.2]

Periodic measurement
Determination of a measurand at specified time intervals. The specified time intervals may be regular (e.g., once every month) or irregular. Measurands can include the amount or physical property of an emission. Measurements are usually made using portable equipment for typically less than 24 h [BS EN 15259:2007, 3.3]

Grid measurement
Determination of a measurand in a given grid of measurement points in the measurement plane [BS EN 15259:2007, 3.4]

Measurement series
Successive measurements of the same measurand carried out at the same measurement plane and at the same process operating conditions.

Measurement site
Place on the waste gas duct in the area of the measurement plane(s) consisting of structures and technical equipment, for example working platforms, measurement ports, energy supply. Measurement site is also known as sampling site [BS EN 15259:2007, 3.11]

Repeatability in the laboratory
Closeness of the agreement between the results of successive measurements of the same measurand carried out under the same conditions of measurement. Repeatability can be expressed quantitatively in terms of the dispersion characteristics of the results. The repeatability is usually expressed as a value with a level of confidence of 95 % [BS EN 15058:2017, 3.26]. Repeatability conditions include:

- same measurement method
- same laboratory
- same measuring system, used under the same conditions
- same location
- repetition over a short period of time

Repeatability in the field
Closeness of the agreement between the results of simultaneous measurements of the same measurand carried out with two sets of equipment under the same conditions of measurement. Repeatability can be expressed quantitatively in terms of the dispersion characteristics of the results. The repeatability under field conditions is usually expressed as a value with a level of confidence of 95 %. [BS EN 15058:2017, 3.27]. These conditions include:

- same measurement method
- two sets of equipment, the performances of which are fulfilling the requirements of the measurement method, used under the same conditions
- same location
- implemented by the same laboratory
- typically calculated on short periods of time in order to avoid the effect of changes of influence parameters (e.g. 30 min)

Uncertainty
Parameter associated with the result of a measurement, that characterises the dispersion of the values that could reasonably be attributed to the measurand [ISO/IEC Guide 98-3:2008, 2.2.3]

Standard uncertainty
Uncertainty of the result of a measurement expressed as a standard deviation [ISO/IEC Guide 98-3:2008, 2.3.1]

Combined standard uncertainty
Standard uncertainty of the result of a measurement when that result is obtained from the values of a number of other quantities, equal to the positive square root of a sum of terms, the terms being the variances or covariances of these other quantities weighted according to how the measurement result varies with changes in these quantities [ISO/IEC Guide 98-3:2008, 2.3.4]

Expanded uncertainty
Quantity defining an interval about the result of a measurement that may be expected to encompass a large fraction of the distribution of values that could reasonably be attributed to the measurand. The expanded uncertainty is usually calculated with a coverage factor of k = 2, and with a level of confidence of 95 %. The expression overall uncertainty is sometimes used to express the expanded uncertainty [SOURCE: ISO/IEC Guide 98-3:2008, 2.3.5]

Uncertainty budget
Calculation table combining all the sources of uncertainty according to EN ISO 14956 or ISO/IEC Guide 98-3 in order to calculate the combined uncertainty of the method at a specified value [BS EN 15058:2017, 3.34]

Maximum permissible expanded uncertainty
Criterion specified for the measurement method to assess the expanded uncertainty associated to a result of measurement.

4 Manual stack sampling method for nitrosamines in PCC.

4.1 Principle

A sample of flue gas is extracted isokinetically through a sample probe and line, before it is passed through three consecutive absorbers housed in an ice bath. The absorbers are filled with 100 mL of 0.1M sulfamic acid aqueous solution to inhibit sample degradation, where the water is the absorbent media and solubility is the main sorbent mechanism. The sample probe and sample line are heated to minimise condensation. However, to prevent any potential thermal degradation of amines to form breakdown products, heating of the sample system is limited to 80 ºC. After the three absorbers filled with the above-mentioned solution, an additional empty impinger (absorber flask) is used to collect most of the further entrainment. Once the test is completed, the solutions are recovered along with washings of the complete system prior to the absorbers and sent for analysis.

Table 1 outlines the list of PCC nitrosamines for analysis following this procedure, the list includes 12 nitrosamines which has been found in PCC (emissions, solvent, or water-wash) all of them having vapour pressures between 0.002 and 0.4 kPa at 20-25 ºC. The listed nitrosamines are ordered by descending vapour pressure

Table 1. Nitrosamines found in PCC with vapour pressures between 0.002 and 0.4 kPa.

Structure	Mass	Formula	CAS	Nitrosamine compound	Acronym
Linear	74	C2H6N2O	62-75-9	Nitrosodimethylamine	NDMA
Linear	88	C3H8N2O	10595-95-6	Nitrosomethylethylamine	NMEA
Linear	102	C4H10N2O3	55-18-5	Nitrosodiethylamine	NDEA
Linear	130	C6H14N2O	601-77-4	Nitrosodiisopropylamine	NDIPA
Linear	130	C6H14N2O	621-64-7	Nitrosodipropylamine	NDPA
Ring (6)	114	C5H10N2O	100-75-4	Nitrosopiperidine	NPIP
Ring (5)	116	C4H8N2O2	39884-53-2	Nitroso-2-methyloxazolidine	NMOx
Ring (5)	100	C4H8N2O	930-55-2	Nitrosopyrrolidine	NPYR
Linear	158	C8H18N2O	924-16-3	Nitrosodibutylamine	NDBA
Linear	158	C8H18N2O	997-95-5	Nitrosodiisobutylamine	NDIBA
Ring (6)	116	C4H8N2O2	59-89-2	Nitrosomorpholine	NMOR
Ring (6)	115	C4H9N3O	5632-47-3	Nitrosopiperazine	MNPZ*

Notes: MNPZ is a nitrosamine and also an amine.
All the listed compounds are secondary nitrosamines

There are another 9 nitrosamines also found in PCC, however, since they have lower volatilities, they are not explicitly included in this method. In principle, additional nitrosamines with lower vapour pressures may also be measured with this method, however the capture efficiency and sample recovery may be reduced, and any attempt of applying the present method to these species should be first tested and validated.

5 Sampling system.

5.1 Reagents

During the analysis, use only reagents of recognized analytical grade. Normal, accepted laboratory safety practices and cleaning procedures for glassware should be followed during reagent preparation.

WARNING – Use the reagents in accordance with the appropriate health and safety regulations.

- Sulfamic acid. Commercially available 99.5%, as solid crystals
- Water. High purity with conductivity $\sigma \approx 10 \mu S/m$
- Methanol. HPLC grade for washing down sampling equipment

5.2 Sampling equipment

A known volume of stack gas is extracted representatively from a duct or chimney at a controlled flow rate. The gas stream passes through the sample probe and connecting tubing and then through a series of absorbers containing absorption solution. All parts of the sampling equipment upstream of the first absorber shall not react with or adsorb nitrosamines. Material used for the construction of sampling systems are typically borosilicate glass, quartz glass, PTFE, or titanium.

5.2.2 Sampling nozzles

A set of sampling nozzles of various sizes to facilitate isokinetic sampling. Constructed of non- reactive/adsorbing material and conforming to the requirements of EN 13284-1.

5.2.3 Sampling probe

A sample probe of sufficient length to reach all of the measurement points required for grid sampling. Constructed of non-reactive/adsorbing material and with the facility to be heated to a controlled temperature of 80oC.

5.2.4 Flow measurement device

To measure the stack gas velocity at all sampling points. Shall fulfil the performance requirements of BS EN ISO 16911-1. To be used to determine the velocity profile of the duct prior to sampling and to be mounted in the duct in such a way as to facilitate continuous measurement of the point velocity during sampling. L-Type Pitot tubes or any other flow measurement device than can get blocked or its readings affected by the presence of droplets shall not be used.

5.2.5 Stack temperature measurement

To measure the stack gas temperature at all sampling points. Shall fulfil the performance requirements of BS EN ISO 16911-1. To be used to determine the temperature profile of the duct prior to sampling and to be mounted in the duct in such a way as to facilitate continuous measurement of the point temperature during sampling.

5.2.6 Absorbers

For efficient absorption three absorbers shall be placed in series. They shall be of a design that promotes efficient dispersion of the sample gas in the absorption solution and maximises the length of the gas path through the solution. They should also be of sufficient capacity to handle isokinetic sampling rates without excessive bubbling which can lead to transfer of solution from one absorber to the next. An empty absorber bottle should be placed after the third absorber and before the drying cartridge to prevent contamination of the drying medium.

5.2.7 Drying cartridge

Filled with a suitable desiccant and mounted downstream of the absorber train to protect sample pump/metering system. Silica gel (1mm – 3mm grain size) is a suitable desiccant. The drying cartridge can be a fifth absorber mounted in the iced water bath.

5.2.8 Iced water bath

The absorber train shall be contained in an iced water bath to promote efficient absorption. The exit temperature of the absorber train shall be maintained at or below 20 ºC for the duration of the test.

5.2.9 Connecting tubing

Ideally the absorber train should be mounted directly behind the sample probe to minimize the length of the gas path. In situations where this is not practical, a length of flexible tubing may be used. This tubing shall be as short as possible, in order to minimise the residence time of the gas. Constructed of non-reactive/adsorbing material, it shall be maintained at the same temperature as the sample probe. Silicone or rubber are not suitable materials as they are known to absorb or react with nitrosamines.

5.2.10 Suction unit

A gas tight pump or similar, to draw the sample through the sample train. Shall conform to the requirements of EN 13284-1 section 7.2.5.

5.2.11 Gas metering system

A system to determine the sampled gas volume temperature, pressure, and sample rate. Shall conform to the requirements of EN 13284-1 section 7.6.
An example of a sampling system is shown in Figure 1.

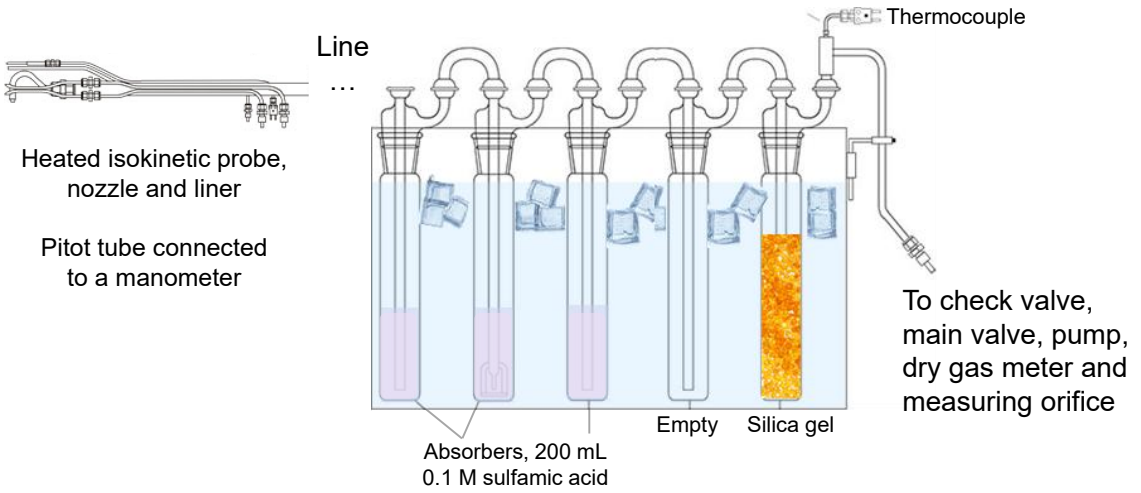

Figure 1. Wet chemical sampling (manual stack sampling) for volatile nitrosamines found in PCC

6 Performance Characteristics

6.1 Performance characteristics and associated performance criteria

6.1.1 General

Table 2 and Table 3 specify the performance characteristics and the associated performance criteria of the whole measurement method. The relevant performance characteristics and the associated performance criteria are deduced from the validation experiments.

The analytical laboratory implementing the measurement method shall demonstrate that:

- performance characteristics of the measurement method given in Table 2 meet the specified performance criteria
- expanded uncertainty calculated by combining values of selected performance characteristics by means of an uncertainty calculation for the actual site conditions does not exceed
- a specified percentage of the daily emission limit value (ELV) or the lowest limit value specified for the plant by the competent authorities
- a fixed absolute value for low measured values.

The values of the selected performance characteristics shall be evaluated:

- for sampling by means of laboratory tests and field tests
- for analysis by means of laboratory tests.

Table 2. Performance characteristics of sampling to be determined in the laboratory (L) and in the field (F) and associated performance criteria.

Performance characteristic	L	F	Performance criterion
Determination of the volume of the absorption solution		X	≤ 1,0 % of the volume of solution
Gas volume meter:			
— standard expanded uncertainty of sample volume [b]	X [a]		≤ 5 % of the volume of gas sampling [a]
— expanded uncertainty of temperature [b]	X [a]		≤ 2 % of the absolute temperature [a]
— expanded uncertainty of absolute pressure [b]	X [a]		≤ 2 % of the absolute pressure [a]
Absorption efficiency [c]		X	≥ 95 %
Leak in the sampling line		X	≤ 2,0 % of the nominal flow rate
Field blank value		X	≤ 10,0 % of ELV

a. Performance criteria corresponding to the uncertainty of calibration.
b. The uncertainty of the sampled volume is a combination of uncertainties due to calibration, drift (random drift, drift between two calibrations) and resolution or reading. The uncertainty of temperature and absolute pressure at the gas volume meter is a combination of uncertainties due to calibration, drift (random drift, drift between two calibrations), resolution or reading, and standard deviation of the mean when several values are used to get the result.
c. This characteristic is a quality assurance check to quantify the absorption efficiency in the first absorber; but it does not quantify a possible loss of absorption, and therefore it is not included in calculation of expanded uncertainty. The absorber efficiency check becomes less effective as the concentration of the pollutant in a stack gas decrease. If the emission concentration of all nitrosamine species is less than 305 of the emission limit value, then the absorption efficiency requirement does not need to be fulfilled.

6.1.2 Performance characteristics of analysis

The analytical laboratory shall identify the sources of uncertainty associated to analysis and shall determine the values of the individual standard uncertainties and when combined (root sum of squares) and expressed as an expanded uncertainty at a 95% confidence interval they shall meet the requirements of Table 3. Main possible sources of uncertainty associated to analysis are:

- performance characteristics of the analysis equipment
- preparation of calibration standards: purity of stock standard solution, and ratio of dilutions
- linearity of calibration curve depending on the extend of working range
- measurement of volume of aliquot solution injected for analysis (ratio of the total absorption solution volume and the volume of the aliquot taken for injection)
- if a dilution of the absorption solution is necessary before analysis: ratio of dilution
- interferences
- drift of retention time
- repeatability.

Table 3. Performance characteristics of analysis to be determined in the laboratory and associated performance criteria

Performance characteristic	Performance criterion
Maximum permissible expanded uncertainty of analysis for a level of confidence of 95 %	<= 20%

6.2 Calculation of measurement uncertainty

The testing laboratory implementing the measurement method shall calculate the measurement uncertainty for the actual field conditions. The measurement uncertainty calculated by the testing laboratory shall be expressed as an expanded uncertainty. Table 2 and Table 3 indicate which performance characteristics shall be included in the calculation of the combined standard uncertainty.

The principle of calculation of the combined standard uncertainty is based on the law on propagation of uncertainty laid down in ISO/IEC Guide 98-3 (GUM):

- determine the standard uncertainties attached to the performance characteristics to be included in the uncertainty calculation according to ISO/IEC Guide 98-3
- calculate the combined standard uncertainty by combining all the standard uncertainties according to ISO/IEC Guide 98-3
- values of standard uncertainty that are less than 5 % of the maximum standard uncertainty may be neglected
- calculate the combined standard uncertainty at the measured value, reported as a dry gas value at actual concentration of oxygen
- calculate the expanded uncertainty by multiplying the combined standard uncertainty with a coverage factor for a level of confidence of 95 % and for the applicable number of degrees of freedom.

The calculation of measurement uncertainty can be based on an uncertainty budget. When the concentration of a measured component must be expressed at an oxygen reference concentration (e.g. 3 % or 11 %), the correction of oxygen can bring an additional uncertainty which could be significant if the difference between the oxygen measured value, and the oxygen reference value is large.

7 Planning

7.1 Measurement planning

Emission measurements at a plant shall be carried out such that the results are representative for the emissions from this plant and comparable with results obtained for other comparable plants. Therefore, measurements shall be planned and documented in a measurement plan in accordance with BS EN 15259.

Before carrying out any measurements, the purpose of the sampling and the sampling procedures shall be discussed with the plant personnel concerned. The nature of the plant process, e.g. steady-state or cyclic, can affect the sampling programme. If the process can be performed in a steady state, it is important that this is maintained during sampling.

Dates, starting times, duration of survey and sampling periods as well as plant operating conditions during these periods shall be agreed with the plant management.

If no suitable location exists in the plant, and/or that measurements have been carried out during non- steady-state conditions of the plant, which leads to an increase of the uncertainty of the measurements, it shall be stated in the measurement report.

The responsibilities of the testing laboratory regarding the interface between sampling and analysis and regarding the presentation of the results shall be specified in the measurement plan.

The responsibilities for either sampling or analysis or for both as well as the interface requirements between these activities should be indicated in the measurement plan. This should address the management activities of the team that is responsible for the whole measurement method and signs the measurement report. The measurement plan

should specify e.g. the necessary QA/QC procedures including the sample handling with respect to sample transportation, sample storage, and sample stability in view of subsequent analysis in the analytical laboratory.

7.2 Sampling strategy

7.2.1 Sampling location

This procedure requires isokinetic sampling at multiple points across the measurement plane. Therefore, consideration shall be made to selecting a suitable location that allows representative sampling, and which can be safely accessed and worked from.

7.2.2 Representative Sampling

Considering where the sampling location shall be located is important to achieve representative sampling. Sample planes where the flue gases are well mixed and there is a homogenous flow are usually well suited. These conditions are usually met when:

- The duct has a uniform shape and cross-sectional area
- In a section of straight duct that is greater than five hydraulic diameters upstream and two hydraulic diameters downstream
- Reasonably far away from any disturbances that could affect the flow

Whilst these parameters should ensure a suitable monitoring location, the following requirements shall be met:

- The angle of the gas flow shall be <15º in relation to the duct axis
- There should be no local negative flow
- The ratio of the velocity, from highest to lowest, shall be no more than 3:1
- The minimum velocity shall be measurable depending upon the technique used

The measurement section shall be situated in a location where a suitable working platform and access ports can be installed.

The number of measurement points required across the sampling plane shall be determined using the procedure described in BS EN 15259 Annex D.

Sample duration shall be considered when carrying out representative sampling. Sufficient mass shall be collected in order to achieve the analytical limit of detection. Sample duration should also take into account process variation over time. In order to obtain a representative sample, the minimum sample duration shall be 5 hours, unless the duration of process operation prohibits this.

7.2.3 Platform Work Area

The working platform shall be of a sufficient size and suitability to carry out sampling safely. Access to the sample ports is required to allow installation of the probe and sample train, as well as suitable clearance to avoid impediment from guardrails. Guidance for working platform requirements and provisions is provided in BS EN 15259.

7.2.4 Safety & Work Environment

Safe access to and at the sampling location is required. Guidance for safety and environmental conditions is provided in BS EN 15259.

7.3 Preparation

The reagents and glassware shall be prepared in a laboratory prior to carrying out a measurement campaign. A suitable amount of reagent shall be prepared to complete the anticipated number of measurements. The glassware and connections/parts prior shall be cleaned to a suitable standard before it is used.

Clean the components using good laboratory practice. After clean rinse each component 3 times with alternating solutions of 0.1M sulfamic acid and methanol. After drying, seal each component to avoid contamination. If the

same set of glassware is to be used to carry out repeat tests it shall be thoroughly cleaned beforehand. All reagents shall be stored in brown glass bottles to protect them from sunlight

8 Field operation

8.1 Pre-Sampling Flow Measurements

Prior to sampling carry out velocity and temperature measurements at the determined grid measurements on the sampling plane. Check that the flue gas flow criteria defined in section 7.2.2 have been met.

8.2 Equipment Setup

8.2.1 Transport the equipment to the sampling location, making sure all parts are sealed to avoid contamination. Depending on the location it may be advisable to prepare the absorbers beforehand.

8.2.2 Determine the waste gas characteristics specified in BS EN 13284 (Section 9.3) in order to determine the appropriate nozzle for isokinetic sampling.

8.2.3 A sample probe with combined flow measurement capabilities shall be used so the isokinetic flow rate can be determined at each sample point.

8.2.4 Mark the sample probe with the pre-determined grid measurement points if this has not been done.

8.2.5 Connect the sample probe to the absorbers and then the glassware to the rest of the sampling system. Assemble the flow measurement system ensuring it reads zero prior to use. It is advisable that the connection between the sample probe and absorbers is as short as possible, in order to minimise the residence time of the gas before reaching the absorbers.

8.3 Absorber Setup

8.3.1 Five absorbers are required. Pour 100g or 100ml of the 0.1M sulfamic acid solution into each of the first three absorbers. The fourth absorber shall be left empty. The fifth absorber shall be filled with approximately 200g of silica gel.

8.3.2 Weigh and record the values for each of the absorbers as well as the glass connections.
This method assumes the presence of droplets in the stack and saturated gas. The requirements of EN 14790: 2017 shall be followed for the determination of water vapour content. Isokinetic sampling of a gas containing droplets can lead to an over estimation of moisture content, in which case the procedure for saturated gas outlined in EN 14790:2017 shall be followed. However, it is good practice to determine the mass increase of the absorbers during sampling to prove (or otherwise) that the gas has remained saturated for the duration of the test and that there no leaks have developed during testing.

8.3.3 Assemble the absorber train and seal until it is ready to be incorporated into the sample system.

8.4 Pitot Tube Leak Check

8.4.1 Ensure the differential pressure readout device display reads zero and apply positive pressure to the impact side of the Pitot tube (to at least as high a pressure as the differential pressure expected during the measurement or to 50 % of the range of the differential pressure readout device whichever is higher). Once sufficient pressure has been applied, ensure the system is sealed and observe the displayed reading. The pressure reading should remain stable for fifteen seconds.

8.4.1 The pressure should remain stable to within ± 25 Pa (for at least 15 seconds). If the displayed pressure reading drops check all connections in the assembly and repeat step 8.4.1. Repeat steps to confirm the static Pitot tube side by applying a negative pressure.

8.4.2 Record the outcome of the Pitot tube leak check on the appropriate field data sheet.

8.5 Sample System Leak Check

8.5.1 Seal the inlet of the sampling system using a suitably clean stopper and turn on the vacuum pump. Open the control valve and gradually increase the flow until the vacuum pressure reaches a level expected during the test.

8.5.2 Once the sampling system has stabilised make a note of the dry gas meter reading and time the leak rate over one minute. The flow rate during the leak test shall not exceed 2% of the expected average flow.

8.5.3 Slowly release the stopper to release the vacuum in the sample system before shutting the control valve off.

8.5.4 If the leak test fails, fix any leaks in the sampling system, and repeat steps 8.5.1 to 8.5.3 until the leak test is passed.

8.5.5 Record the outcome of the sample system leak check on the appropriate field data sheet.

8.6 Sampling

8.6.1 Before testing can begin, ensure all parts of the sampling system where the sample gas is exposed to sunlight are covered up. Sunlight can degrade the collected sample and therefore care must be taken throughout the testing and recovery to avoid exposure.

8.6.2 Prepare the field data sheet and calculate the isokinetic sample rate. Record the dry gas meter start volume and barometric pressure.

8.6.3 Carefully install the probe into the measurement port and move it to the first measurement point making sure the nozzle is facing the direction of the incoming flue gas.

8.6.4 Wait until the flow measurements have stabilised and calculate the required sampling rate. Make a note of the time, start the timer and the pump. Adjust the flow rate until the required sampling rate has been achieved.

8.6.5 Record the flue gas flow rate (differential pressure), sample flow rate, stack temperature, dry gas meter temperature, last absorber exit temperature and vacuum pump pressure.

8.6.6 Once the required amount of time has elapsed, move the sample probe to the next measurement point and adjust the flow rate to maintain isokinetic sampling conditions. Record the same parameters in step 8.6.5 in the field data sheet.

8.6.7 These parameters shall be recorded at each measurement point and at least every five minutes.

8.6.8 It is important to maintain isokinetic sampling conditions of between 95% and 115% during the entire sampling duration.

8.6.9 Repeat steps 8.6.6 and 8.6.7 until all measurement points have been tested.

8.6.10 Turn off the sample pump and remove the probe from the stack.

8.6.11 Repeat the leak test in steps 8.5.1 to 8.5.3 at the highest vacuum pressure recorded during the test. The test is valid if a leak rate of 2% or less of the flow rate is achieved.

8.7 Sample Recovery

8.7.1 Disassemble the sample train and seal the absorbers taking care to not expose them to sunlight.

8.7.2 Pre-weigh two brown glass sample bottles and record their weight.

8.7.3 Thoroughly rinse the sample system up to the first absorber, i.e., the nozzle, probe, and connection to the absorbers, 3 times in the following sequence:

0.1M Sulfamic acid, Methanol, 0.1M Sulfamic acid

Collect the washings in the first sample bottle.

8.7.4 If the sample train is to be reused, perform an additional rinse as specified in 8.7.3. This rinsing solution shall be collected and stored. It shall be analysed if the subsequent test exceeds the emission limit value. Seal the ends of each rinsed component ready for the next test.

8.7.5 Begin the recovery of the absorbers by moving them to an area away from direct sunlight and re-weigh each of the absorbers and connectors, record the results.

8.7.6 Empty out the contents of the first absorber into the first sample bottle. Thoroughly rinse out the first absorber and associated glass connector with DI water three times and add the resulting washings to the same bottle.

8.7.7 Empty out the contents of the second absorber into the first sample bottle. Thoroughly rinse out the second absorber and associated glass connector with DI water three times and add the resulting washings to the same bottle.

8.7.8 Empty out the contents of the third absorber into the second sample bottle. Thoroughly rinse out the third absorber and associated glass connector with DI water three times and add the resulting washings to the same bottle.

8.7.9 Rinse out the fourth empty absorber with DI water three times and add the resulting washings to the second sample bottle.

8.7.10 Weigh and label each of the sample bottles. Record the volume and fill out a chain of custody form.

8.8 Sample Handling & Storage

8.8.1 Samples shall be stored in amber glass bottles to protect them from sunlight.

8.8.2 The bottles must be stored in a fridge and kept below 6 ºC.

8.8.3 The samples shall be despatched to the analysis laboratory within 14 days and stored at the same conditions throughout shipment.

8.8.4 Samples shall be shipped with a chain of custody and the relevant material safety data sheet.

8.8.5 A temperature datalogger shall be sent with the samples to the analysis laboratory to provide confirmation that the samples were stored below 6 oC during transit.

8.9 Field Blank

8.9.1 A blank shall be carried out at least once per sample location during a measurement campaign.

8.9.2 Setup the sampling system as described in steps 8.2, 8.3 and 8.5.

8.9.3 Do not put the sample probe in the stack.

8.9.4 Disassemble the system and recover the sample in accordance with step 8.7.

8.9.5 The blank shall be reported separately. If a measured result is less than the blank, the result shall be reported as equal to or less than the blank.

8.10 Sample analysis

There is no standard method used to analyse liquid samples for nitrosamines. Either gas or liquid chromatography is typically used (depending on the species) coupled with an analyser (FID, MS, TEA, etc.), which may include a pre-treatment.

9 Calculations and expression of results

The mass of each measured nitrosamine collected in the samples shall be reported. The final emission concentration result for each species will be derived from the analysis of several samples (sample train wash, absorbers 1&2, absorbers 3&4). Some of these samples may be below the analytical limit of detection while others may yield positive results for the same species. Therefore, two sets of results for each species for each test shall be reported. One set where all results below the limit of detection are assumed to be zero, and a second set where all results below the limit of detection are assumed to be at the limit of detection. The sample gas volume shall be used to calculate the measured concentration.

9.1 Calculations

9.1.1 Determining Gas Volume at Standard Conditions

$$Vol_{corr} = Vol_{Meas} \frac{273.15}{T} \frac{P}{101.3}$$

Where: Vol_{Corr} is the corrected gas volume at standard conditions
Vol_{Meas} is the measured gas volume
T is the temperature of the gas meter in Kelvin
P is the pressure at the gas meter in kPa

9.1.2 Determining the Measured Concentration for each species

$$C = \frac{M}{Vol_{corr}}$$

Where: C is the measured concentration of the nitrosamine
M is the mass of nitrosamine collected for this species

9.1.3 Determination of Absorption efficiency

The absorption efficiency shall be determined for each test for each nitrosamine compound. The combined mass of analyte collected in the probe wash and absorbers 1 & 2 is compared with the mass collected in the whole sample train (including absorbers 3 & 4) and expressed as a percentage.

$$\text{Efficiency} = (M_1/M_T)*100\%$$

Where: M_1 is the combined mass in the probe wash and Absorbers 1 & 2
M_T is the total mass collected in absorbers 1, 2, 3 & 4 plus the probe wash sample

9.2 Expression and assessment of results

The result of measurement shall be expressed with the corresponding expanded uncertainty for a level of confidence of 95 %.

The field blank value shall be less than 10 % of the emission limit value (ELV). The field blank value shall not be subtracted from the measured value. If the calculated measured value is less than the previously determined field blank value, the result of measurement shall be reported as less or equal to the field blank value. The field blank value shall be reported.

10 Measurement report

The measurement report shall provide a comprehensive account of the measurements, a description of the measurement objective and the measurement plan. It shall provide sufficient detail to enable the results of measurement to be traced back through the calculations to the collected basic data and process operating conditions.

The measurement report shall include the items specified in BS EN 15259 and at least the information on the following items:

a) Information about the personnel involved in the measurement
b) Description of the location of the measurement points in the measurement plane
c) Changes in the plant operations during sampling
d) Characteristics of the sampling equipment
e) For each measurement; sampling date, time, and duration as well as identification of samples
f) Measurement results of each nitrosamine measured: sampling volumes, concentrations
g) Blank values for each nitrosamine
h) Absorption efficiency for each nitrosamine

11 References

EN 15259:2007, Air quality — Measurement of stationary source emissions — Requirements for measurement sections and sites and for the measurement objective, plan and report.

EN 13284-1:2017, Stationary source emissions — Determination of low range mass concentration of dust.

EN ISO 16911-1:2013, Stationary source emissions — Manual and automatic determination of velocity and volume flow rate in ducts.

21GRD06 MetCCUS

ANNEX 3. Deliverable 3.

PERFORMANCE ASSESSMENT OF A MONITORING METHOD FOR VOLATILE NITROSAMINES STACK EMISSIONS IN AMINE BASED POST COMBUSTION CO_2 CAPTURE.

Authors: H. Barros, R. Harvey, H. Cheales-Norman, C. Dimopoulos, R. Robinson.

Lead participant: **NPL**

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1	NPL National Physical Laboratory	Hampton Rd, Teddington TW11 0LW. London. UK.

Summary

This report forms a part of the project EURAMET / MET CCUS, and is addressing the activity 2.1, Task 2.1.4.

This report on requirements for amine-based PCC stack emissions monitoring is meant to provide guidance to regulatory bodies, monitoring contractors, industry and other parties interested in stack emission monitoring associated to CCUS. Also, it contains a survey in the emissions levels reported in the literature for amines and nitrosamines in PCC.

This report summarises the results on a systematic performance assessment of the method described in the Task 2.1.2 report specifically designed to monitor volatile nitrosamine emissions from Post Combustion Capture (PCC) plats stacks. The present validation test series was performed under simulated controlled conditions mimicking PCC stack conditions (temperatures, post capture flue gas compositions, etc.) using a purpose made test rig developed at NPL. This validation data has been recently reported [Barros et al. 2025].

The aqueous samples for this test were obtained by means of a series of liquid (water with 0.1 M sulfamic acid) impingers, while additional dry cartridges were used to check for nitrosamines breaking through the sampling system. The nitrosamine concentration laboratory analysis was performed by GC-TEA (Gas Chromatography coupled to Thermal Energy Analysis). However, any other previously validated lab-based analytical technique could be used provided their capacity to identify and measure the relevant compounds.

The liquid impinger sampling recoveries range from 75 to 100 % for individual nitrosamines. The impinger efficiencies depend on the volatility and chemical structure of the specific nitrosamines. Two different criteria were used to assess the validity of the method, the known amounts of injected nitrosamines and a capture efficiency criterion of 95% which is typical for wet chemistry stack emission measurement methods.

The developed method could be used for other nitrosamine species with similar volatilities and structures to those here tested, as far as they have volatilities within the tested range (vapour pressures from 0.005 to 0.4 kPa). This method has not been validated for low volatile nitrosamines, such as NDELA and EHEN, which has been also found in PCC plants. These kind of compounds behave differently and may require different sample media and/or independent validation in order to be sampled, for that reason they are not part of the scope of this report.

Finally, stack conditions may vary for different PCC plants, and they may be different to the conditions simulated during the present laboratory testing. In those cases, it is advisable to assess the impact of such changes on the proposed method efficacy.

Table of Contents

1 Selected nitrosamines and used reference standard material

Table 1 summarises the list of nitrosamines used in the present test. These were selected to cover the range of vapour pressure from 0.005 to 0.4 kPa (values at 20 ºC). This group encompass the volatile and some of the semi-volatile nitrosamines. It is worth nothing that amongst the nitrosamines found in PCC plants NDMA (VP = 0.4 kPa @ 20 ºC) is the most volatile one, while there are several nitrosamines with lower volatilities than the lower limit chosen for the present validation exercise (see Task 2.1.2 report).

Table 1. Nitrosamines selected for the present validation exercise and some of their properties.

Compound	CAS #	VP @ 20 ºC	Solubility in water (g/L)	Other solubilities
NDMA	62-75-9	0.4	100 to 1000	alcohols, ether, ethyl ether, chloroform. Lipids.
NMEA	10595-95-6	0.15	Not miscible or 300g/L	Chloroform (sparingly), ethyl acetate & methanol (slight)
NDEA	55-18-5	0.11	100 to 106	Organic solvents, lipids
NDPA	621-64-7	0.030	Not miscible or 9.9g/L	Alcohol; ether; organic; lipids
NPIP	100-75-4	0.012	10 to 77	Organic solvents and lipids, HCl
NDBA	924-16-3	0.006	1.27 to 120	Organic solvents
NPYR	930-55-2	0.005	53 to 1000	Organic solvents and lipids. Methanol (slightly)
NMOR	59-89-2	0.005	100	Organic solvents

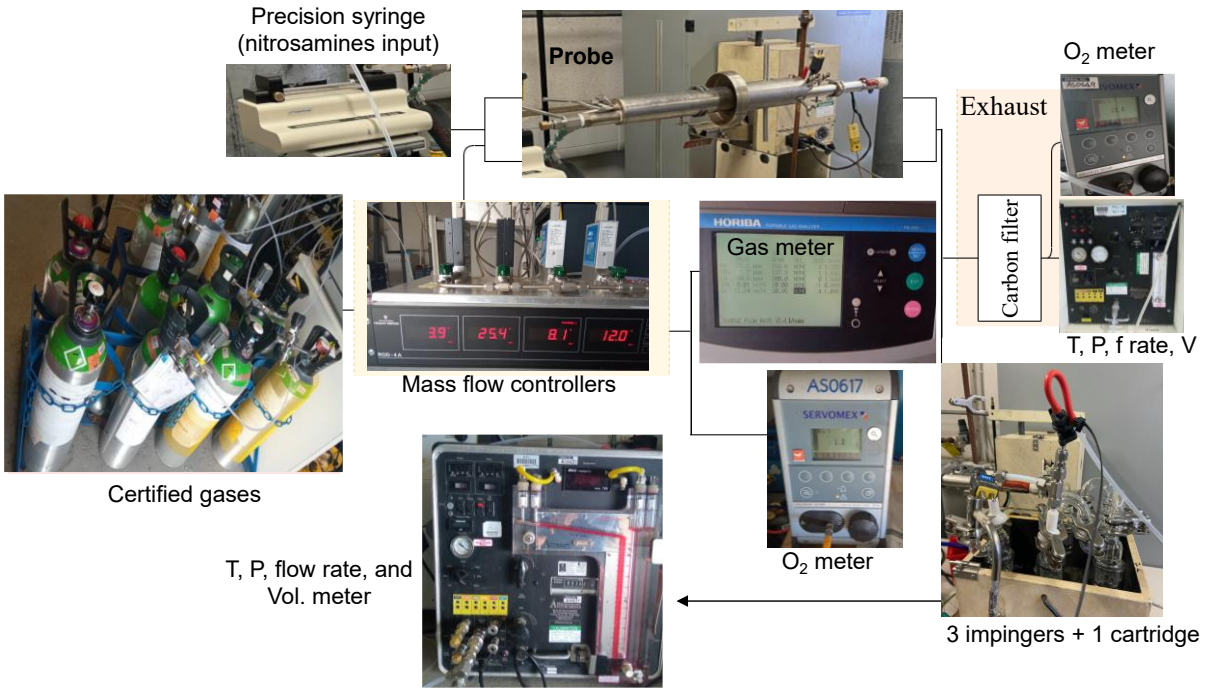
The nitrosamines were injected in the testing system using a purpose made solution obtained by dilution of the EPA 8270/Appendix IX Nitrosamines Mix. reference standard, which contains a cocktail of all the mentioned nitrosamines at the same concentration (about 2000 µg/mL each) in a methanol matrix. The tracing solution was diluted to produce the different tracing aliquots, with the desired concentrations, to be used during the method validation. The used solution contained approximately the same concentration for each nitrosamine species.

2 NPL test bench for PCC nitrosamine manual sampling method performance assessment and test series description.

Typical PCC post-capture flue gas conditions were simulated in the experimental bench. All the gas flows and conditions were carefully controlled (Figure 1). A series of 3 impingers were used to capture the target analytes exiting the experimental system. Here after we will call I1 the first liquid impinger, I2 the second and I3 the last one. All the impingers where filled with approx.. 200 mL of a 0.1 M sulfamic acid solution. A Thermo-Sorb cartridge was placed at the back end of the capture system in order to capture any possible breakthrough of nitrosamines.

After each test the impingers and the water coming from the probe rinse (labelled as PW – probe wash) were collected, the last is necessary to measure any nitrosamine amounts deposited on the glassware surfaces. Due to the oily/sticky nature of nitrosamines the full efficiency of the wash can't be guaranteed. This cleaning process is made by hand, as required for any stack method, so it cannot be done at high temperature.

The equipment selected and used (measurement devices, heated lines, flow rate meters, etc.) are the same instruments generally used on field works with the actual PCC stacks. The following picture series illustrates some of those and the general assembly of the rig.



Picture 1. Equipment used in the nitrosamine liquid sampling method test bench.

3 Performance assessment of the nitrosamine chemical sampling (manual sampling) and monitoring method in simulated PCC stacks conditions: test series description.

The used gas mixtures where made up using certified cylinders of high purity gases carefully blended with mass flow controllers calibrated to secondary standards. Synthetic dry air was obtained by a purpose made scrubber system and humidity was added from a system feed by deionised water. The gas stream composition included NOx (72 ppm of NO and 7 ppm of N_2), CO (21 ppm) and SO_2 (5.7 ppm), which are usually encountered in flue gases. The nitrosamines where injected using an automatic precision syringe at a rate of 0.05 mL per minute, to deliver 3 mL of the nitrosamine traced solution along the test duration (one hour each). For the blank tests, pure water injection at the same rate was used.

A total of fifteen tests, T1 to T15, were performed at the same temperature (about 80 °C) and at a pressure slightly above the atmospheric pressure. All the tests were performed using the same blend of 8 nitrosamines. The test plan is summarised below:
T1 blank (day 1)
T2 nitrosamine injection (day 2)
T3 nitrosamine injection (day 2)
T4 blank (day 3)
T5 nitrosamine injection (day 4)
T6 nitrosamine injection (day 5)
T7 blank (day 5)
T8 nitrosamine injection (day 5)
T9 blank (day 9)
T10 -T14 nitrosamine injection (day 10)
T15 nitrosamine injection (day 12)

For each test a nitrosamine mass of 6 to 7.4 micro grams (per species) was injected into the test bench, this represented a concentration of approximately 7 µg/m^3 of each nitrosamine, bubbled through the impingers at a constant rate of 14-15 L/min for one hour.

This test focused on the repeatability of the test series performed in fixed conditions during this experimental phase. The present series of experiments allow direct comparability of the results. Practically identical gas conditions and the same amount of nitrosamines were used in all the tests. Temperature of the probe and the heated sampling line was 80 ºC, maintained below the dew point to allow the presence of water vapour droplets.
The main gas stream was split in two using a T connector and a valve. A reduced stream (approx. 10% of the flow) was diverted to a Thermo-Sorb/N cartridge, which has an operational flow rate in the range of 0.2 - 4 L/min. The other 90% of the gas stream was used for the wet sampling method (impingers). Thermo-Sorb/N cartridges were used at the end of each impinger series, in order to collect and quantify the possible nitrosamine breakthrough.

Finally, as an additional safety feature, two consecutive filters with activated carbon filters (1,5 L each) were plugged at the end of the system to avoid the dispersion of the nitrosamines potentially braking through the whole system.

The samples were refrigerated after sampling. Also, the samples were kept cold in thermally insulated boxes with ice packs during shipment to the analytical laboratory and temperature was verified by temperature loggers. The maximum recorded temperature was 10 °C, but this only occurred close to the arrival time. The samples were analysed by Gas Chromatography coupled to a Thermo-Energy Analyser (GC-TEA).
The blank test (T1) registered values below the analytical method detection limit, equivalent to ≈ 0.05 µg of each nitrosamine for the liquid samples and equal to 4 ng within the Thermo-Sorb cartridges.

4 Results of the nitrosamine manual sampling and monitoring method under simulated PCC stacks conditions

All the liquid samples were quantified in µg/L. However in the summarised data tables presented in this report we reported the corresponding masses (µg) of captured nitrosamines, these were calculated considering the volumes used in each test. Measurements of the nitrosamine amounts captured by the Thermo-Sorb/N cartridges located at the back of the system are also reported in µg.

In the data tables presented in this section, we adopted the following notation.

- I1, I2 and I3 corresponds impingers 1, 2 and 3 respectively
- PW stands for Probe Water (after washing probe and impingers)
- TC means back end Thermo-Sorb cartridges
- Values below the lower limit of detection (LOD) were left in blank
- Vol. [mL] is the volume of the sample collected in each impinger or probe water
- Nom. stands for Nominal Mass, the amount of individual nitrosamine injected in each test
- Thermo-Sorb values were corrected by the used dilution factor, representing the mass of nitrosamines breaking though the impinger system

Table 1. Results for the blanks in the Liquid Sampling Method test (µg).

	T1				T4				T7				T9			
Specie	I1	I2	I3	PW	I1	I2	I3	PW	I1	I2	I3	PW	I1	I2	I3	PW
LOD	0.05	0.04	0.05	0.05	0.04	0.04	0.04	0.09	0.05	0.04	0.04	0.01	0.05	0.04	0.05	0.01
NDMA					0.10				0.06				0.08			
NMEA					0.07								0.06			
NDEA																
NPIP					0.13				0.052				0.05			
NDPA																
NDBA										0.06						
NPYR					0.33			0.11	0.07				0.10			0.03
NMOR					0.35			0.12	0.06				0.09			0.03
Vol [mL]	245	212	254	52	205	207	183	86	227	211	219	56	249	206	245	56

Notes: - Nitrosamines in I1 (blank tests) are remains from the previous traced tests
- Thermo-Sorb cartridges values were systematically below the LOD (0.004 µg)

Table 2. Test 2 & 3 results: Liquid Sampling Method.

	T2						T3					
Specie	I1	I2	I3	PW	TC	Nom.	I1	I2	I3	PW	TC	Nom.
LOD	0.05	0.04	0.05	0.03	0.02		0.05	0.04	0.05	0.03	0.05	
NDMA	5.0	1.7	0.3	0.06	0.07	6.5	6.2	1.1	0.3	0.3		6.4
NMEA	5.2	2.1	0.4		0.11	6.5	6.6	1.5	0.4	0.2		6.4
NDEA	4.5	1.7	0.7		0.22	6.5	6.4	1.9	0.7	0.1	0.18	6.4
NPIP	5.0	1.4	0.2	0.11		6.6	4.7	0.9	0.2	0.4		6.4
NDPA	3.3	3.1	1.2		0.51	6.5	5.0	2.3	1.1	0.2	0.23	6.4
NDBA	1.7	2.5	1.3		0.86	6.5	2.8	2.1	1.4	0.1	0.47	6.4
NPYR	4.3	0.8	0.1	0.39		6.5	1.9	0.2		0.9		6.4
NMOR	4.3	0.8	0.1	0.39		6.5	1.7	0.2		0.9		6.4
Vol [mL]	237	192	246	32			237	192	246	32		

Table 3. Test 5 & 6 results: Liquid Sampling Method.

	T5						T6					
Specie	I1	I2	I3	PW	TC	Nom.	I1	I2	I3	PW	TC	Nom.
LOD	0.04	0.05	0.05	0.1	0.04		0.06	0.05	0.04	0.02	0.004	
NDMA	5.3	0.9	0.1			6.8	5.34	0.77	0.18			6.1
NMEA	5.5	1.2	0.2			6.8	5.34	0.93	0.13			6.1
NDEA	4.9	1.8	0.4			6.8	5.06	1.36	0.24		0.04	6.1
NPIP	5.1	0.7	0.1			6.8	5.91	0.64	0.06			6.1
NDPA	3.6	2.6	0.7		0.16	6.7	3.94	2.09	0.58		0.12	6.1
NDBA	1.6	2.3	1.2		0.45	6.8	2.08	2.27	1.09		0.35	6.1
NPYR	4.5	0.4		0.3		6.8	4.50	0.27		0.05		6.1
NMOR	4.3	0.4		0.3		6.8	5.34	0.34		0.05		6.1
Vol [mL]	197	235	238	113			281	227	222	85		

Table 4. Test 8 & 10 results: Liquid Sampling Method.

	T8						T10					
Specie	I1	I2	I3	PW	TC	Nom.	I1	I2	I3	PW	TC	Nom.
LOD	0.05	0.04	0.06	0.02	0.004		0.04	0.04	0.05	0.01	0.004	
NDMA	4.34	0.58	0.07	0.51		6.1	4.02	0.87	0.14	0.91		6.7
NMEA	4.56	0.77	0.11	0.45		6.1	4.02	1.17	0.22	0.78		6.6
NDEA	4.34	1.11	0.19	0.34		6.1	3.57	1.67	0.44	0.58		6.6
NPIP	4.79	0.51	0.06	0.68		6.1	4.46	0.71	0.09	1.36		6.7
NDPA	3.65	1.71	0.44	0.24	0.10	6.1	2.46	2.18	1.04	0.41		6.6
NDBA	2.28	2.03	0.86	0.17	0.04	6.1	1.09	1.77	1.60	0.29		6.6
NPYR	3.42	0.21		1.07		6.1	2.90	0.22		2.34		6.6
NMOR	3.88	0.28		1.22		6.1	2.90	0.24		2.79		6.7
Vol [mL]	228	214	278	76			223	198	242	65		

Table 5. Test 11 & 12 results: Liquid Sampling Method.

	T11						T12					
Specie	I1	I2	I3	PW	TC	Nom.	I1	I2	I3	PW	TC	Nom.
LOD	0.05	0.04	0.05	0.01	0.004		0.05	0.04	0.05	0.010	0.004	
NDMA	5.07	0.54	0.07	0.35		6.2	6.82	1.78	0.09			7.4
NMEA	5.07	0.69	0.09	0.23		6.2	6.36	2.33	0.10		0.05	7.4
NDEA	5.07	1.01	0.16	0.11		6.2	5.00	2.96	0.18		0.15	7.4
NPIP	4.54	0.47	0.05	0.69		6.2	7.50	1.29	0.06			7.4
NDPA	4.54	1.55	0.33	0.05		6.1	2.73	3.81	0.36		0.47	7.4
NDBA	2.94	1.92	0.67	0.04		6.2	0.64	2.96	0.68		1.22	7.4
NPYR	2.14	0.15		1.77		6.2	7.50	0.53	0	0.013		7.4
NMOR	2.03	0.16		2.02		6.2	7.73	0.57	0	0.013		7.4
Vol [mL]	267	216	257	63			227	212	226	48		

Table 6. Test 13 & 14 results: Liquid Sampling Method.

	T13						T14					
Specie	I1	I2	I3	PW	TC	Nom.	I1	I2	I3	PW	TC	Nom.
LOD	0.05	0.04	0.05	0.01	0.004		240	202	255	62		
NDMA	6.14	0.74	0.07	0.04		6.1	0.05	0.04	0.05	0.01	0.004	
NMEA	5.91	0.91	0.11	0.03		6.1	5.75	1.46	0.25	0.10		6.9
NDEA	5.68	1.25	0.19	0.02		6.1	5.27	1.86	0.41	0.07	0.05	6.9
NPIP	5.91	0.70	0.06	0.06		6.1	4.08	2.43	0.84	0.04	0.15	6.9
NDPA	4.55	1.76	0.38	0.01	0.08	6.1	6.23	1.05	0.14	0.15		7.0
NDBA	2.73	2.07	0.77	0.01	0.20	6.1	2.06	2.83	1.81	0.02	0.52	6.9
NPYR	5.23	0.38		0.12		6.1	0.41	1.50	2.14	0.01	1.50	6.9
NMOR	5.45	0.42		0.13		6.1	5.27	0.36		1.00		6.9
Vol [mL]	227	212	226	48			5.27	0.38		0.55		6.9

Table 7. Test 15 results: Liquid Sampling Method.

	T15					
Specie	I1	I2	I3	PW	TC	Nom.
LOD	249	234	277	62.9		
NDMA	0.05	0.05	0.06	0.01	0.004	
NMEA	5.72	0.87	0.11	0.08		6.2
NDEA	5.72	1.08	0.12	0.05		6.2
NPIP	5.47	1.45	0.22	0.03		6.2
NDPA	5.97	0.77	0.07	0.13		6.3
NDBA	4.48	2.01	0.44	0.02	0.10	6.2
NPYR	2.74	2.29	0.83	0.02	0.29	6.2
NMOR	5.22	0.44		0.33		6.2
Vol [mL]	5.47	0.47		0.35		6.2

5 Recoveries and data analysis of the nitrosamine manual sampling and monitoring method under simulated PCC stacks conditions

The recovery of each one of the 3 impingers, the WP (wash of the probe), back cartridge and the total impinger recovery were analysed. Two different criteria were applied to assess the recovery of the tested wet sampling method, and the results are discussed considering individual nitrosamine properties. The analysis include a discussion on how the different species distribute along the test system.

5.1 Criterium 1: recovery assessment in terms of the mass of nitrosamines injected per test.

Measurements were reported as nitrosamine mass (µg) collected in each test for individual impingers (I1, I2 and I3), PW and TC. Then, for this criterium they are presented as mass percentage, where 100% represents the total amount of nitrosamines injected during each test.

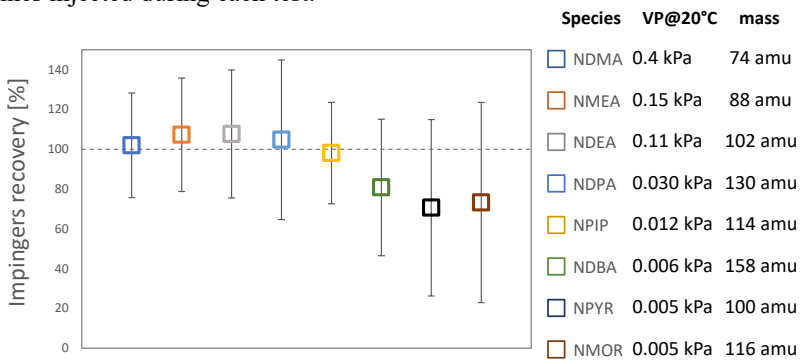


Figure 2. Total impinger recovery for each tested nitrosamine.

The total impinger efficiency is shown in Figure 2, where the sum of the 3 impingers is indicating the yield of the whole liquid sampling system. The 3 nitrosamines with lower volatility are partially captured within the liquid sampling system, achieving a recovery around 75 - 80% (in average). Adding the nitrosamines recovered during the probe wash (PW) and the ones captured by the dry cartridges it will be obtained a plot similar to Figure 2 (not shown). The 5 most volatile nitrosamines will be 105 – 110% while the 3 least volatile nitrosamines will be 80 - 90%. Since this percentage is related to the total amount of injected nitrosamines, this is likely to be related to an analytical overestimation. Table 8 presents the date used to build up the plot in Figure 2.

Table 8. Individual impingers, PW and TC recoveries for each test.

Nitrosamine	Impinger 1		Impinger 2		Impinger 3		PW		TC	
acronym	Ave. %	±2σ	Ave. %	±2σ	Ave. %	±2σ	Ave. %	±2σ	Ave. %	±2σ
NDMA	84	24	15.6	10.4	2.4	3	3.2	9	0.1	0.6
NMEA	84	24	20.1	14.8	3.2	4	2.6	8	0.3	1
NDEA	76	28	25.9	14.2	5.8	7	1.8	6	1	2.6
NDPA	57	34	36	16.2	11.8	14	1.3	4	3.1	5.9
NPIP	84	24	12.6	8.2	1.5	2	5.1	13		
NDBA	30	30	33.3	10.6	17.5	13	0.8	3	7.3	14.2
NPYR	65	44	5.5	5.2	0.1	1	11.7	23		
NMOR	67	50	6	5.6	0.2	1	12.5	28		

5.2 Criterium 2: the absorber efficiency check of each test.

A general practice used in stack monitoring manual extractive techniques is the "absorber efficiency check", which is passed if less than 5% of the measured pollutant is in the last impinger of the sample train", as described in the *Performance standard for organisations carrying out manual stack emission monitoring* [Environment Agency. January 2019]. This is a practical criterium used in actual stacks, where no information about the total amount of nitrosamines is available. Therefore, in this case the 100% is related to the sum of the 3 impingers + the PW (since following this guidance document the dry cartridge at the back end of the system is not part of the requirements).

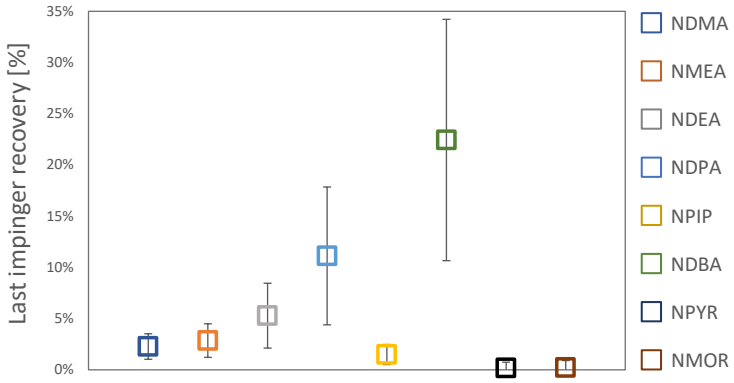


Figure 2. Absorber efficiency check - last impinger recovery.

The nitrosamines NDPA and NDBA have been captured in large amounts in the last impinger, failing the absorber efficiency check. The other nitrosamines have ≤ 5% breakthrough into the last impinger (on average) and using this second criterion they are considered as well captured using this sampling method.

Table 9. Nitrosamines collected in the last impinger.

Nitrosamine	3rd impinger yield
NDMA	2.3 ± 1.2 %
NMEA	2.9 ± 1.6 %
NDEA	5.3 ± 3.2 %
NDPA	11 ± 7 %
NPIP	1.5 ± 1.0 %
NDBA	22 ± 12 %
NPYR	0.2 ± 0.6 %
NMOR	0.2 ± 0.7 %

In all the tables and figures (including Figure 2) the nitrosamines are ordered by its vapour pressure value. So, Figure 2 shows that the lower the volatility (vapour pressure) the larger the absorption on the impinger 3. However, this rule is not followed by the ring type compounds, NPIP, NPYR and NMOR, which are the only species practically non collected in the 3rd impinger. On the other hand, linear nitrosamines having the lowest volatility (NDPA and NDBA) are the ones exhibiting higher values in this last impinger. This is a factor to be kept in mind when applying this method to other nitrosamines (and perhaps amine) species.

Ring type nitrosamines (NPIP, NPYR and NMOR) were partially trapped within the measurement system (probe, piping and/or impinger walls) and then recovered during the washing procedure (PW). The last can be confirmed looking at the PW values in Table 8.

Significant amounts of linear nitrosamines with lower volatility (NDPA and NDBA) can pass through the impingers to the back cartridge. This can be seen also in Table 8, where the probe wash solutions for these two nitrosamines exhibits the larges values. Finally, it is clear that if the ring type nitrosamines are not reaching well the 3rd impinger, it is natural that their values in the back end cartridge are all below the LoD of the method.

6 Conclusions and final comments

A test bench for nitrosamine's sampling test at laboratory scale was developed and tested, this can be used to carefully control all the relevant parameters to mimic the behaviour of an industrial PCC stacks.

The liquid sampling recovery ranges 70 – 110 % for individual nitrosamines, while the repeatability exhibit a large variability even under controlled conditions.

The recovery depends on the volatility of the specific nitrosamines, as expected, but it also it is expected their dependence on the nitrosamine's solubility

The ring-type nitrosamines have lower recoveries as compared with linear ones with similar volatilities.

Cross contamination was observed to be an important factor for the ring type nitrosamines, and a better probe/impinger cleaning method would be necessary (perhaps using a solvent instead pure water).

Based on the known amounts of injected nitrosamines, five species were well sampled, NDMA, NMEA, NDEA, NPIP and NDPA, while NDBA, NPYR and NMOR were sampled at 70 - 80%.

Using the absorber efficiency check only 2 linear nitrosamines with intermediate volatility (NDBA and NDPA) do not pass the check, as they are significantly present in the last impinger. The absorber efficiency check does not match perfectly to the results obtained using the traced amounts of nitrosamines, making challenging a suitable recovery evaluation base on the field data.

The present conclusions can potentially be used for other nitrosamines with similar volatilities (vapour pressure) and similar structures (linear or ring type). However, there are several nitrosamines having much lower vapour pressure values, and these are expected to behave in a completely different manner to the nitrosamines studied here. For that reason, further research is required to validate suitable methods for those species (e.g. NDELA, EHEN etc.).

The stack conditions during a PCC plant operation may differ to the conditions used here, also those conditions may vary across time. Therefore, it is advisable to validate the proposed methods for any condition departing significantly from the ones presented here.

7 References

Environment Agency, UK. Technical Guidance Note (Monitoring) M16, Version 5, Nov. 2016. https://assets.publishing.service.gov.uk/media/5a80160ee5274a2e87db7c54/LIT_6920.pdf.

H Barros; R. Harvey; H. Chales-Norman; C. Dimopoulos; R. Robinson. 2025. Volatile nitrosamine manual stack monitoring method: sampling validation and performance assessment on stack simulated conditions. Carbon Capture Science & Technology. Vol 17, December 2025, 100539. https://doi.org/10.1016/j.ccst.2025.100539.

21GRD06 MetCCUS

ANNEX 4. Deliverable 3.

SIMULATION OF TYPICAL COMPOSITIONS OF POST COMBUSTION CAPTURE CO_2 PLANTS FLUE GAS MATRICES USING NPL'S STACK SIMULATOR AND PROOF OF CONCEPT FOR MEASUREMENTS OF CO_2 USING AERIS MIRA CO_2/N_2O ANALYSER

Authors: Hannah Cheales-Norman, Richard Harvey, Haydn Barros

Lead participant: **National Physical Laboratory**

Due date of the deliverable: 31 July 2025
Actual submission date of the deliverable: 28 October 2025

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1	NPL National Physical Laboratory	National Physical Laboratory Hampton Road Teddington Middlesex TW11 0LW United Kingdom

Summary

With the push towards Net-Zero, there is a need to reduce the release of potent greenhouse gases (GHG) to atmosphere. The combustion of hydrocarbons and organics for the production of energy is one of the largest contributors to the annual release of GHG to atmosphere, with carbon dioxide being the largest pollutant within this sector. Amine-based Post-combustion Carbon Capture (PCC) is the most widely used method in which the contribution of CO_2 released to atmosphere is reduced. Whereby, amine solvents are used to scrub the carbon dioxide from the flue gas. Due to the removal of CO_2, the flue gas matrix composition result in concentrations of carbon dioxide less than that founding the standard post combustion flue gas. These relatively low concentrations can present a challenge to current flue gas analyse standard methods, which were formulated for the use in analyse of flue gases with concentrations of CO_2 one or two orders of magnitude larger.

Building upon the work of 2.1.3 and 2.2.6, this report forms part of the project EURAMET / MET CCUS and is addressing the activity 2.1, Task 2.1.5. The NPL Stack Simulator, a custom built structure in which the extreme conditions within stacks can be simulated in a controlled, scientific manner, was used for producing the results of the present report. A range of typical compositions of post carbon capture flue matrices was produced, and direct measurements were taken by a standard FTIR unit and by the Aeris Mira CO_2/N_2O analyser with the intent to assess its viability as a measurement method.

Contents

1 Introduction

Currently, there are available technologies for monitoring the carbon dioxide emissions from industrial plants. However, these technologies have been developed / optimised for the range of CO2 concentrations of interest in those areas. Table 1 summarises the typical concentration ranges of CO_2 emissions in industrial stack emissions, based on a non exhaustive review of some updated sources. The table includes various fuel types and plant types.

Table 1. Typical industrial carbon dioxide emissions.

Industrial Plant	Type of Fuel	Emitted CO_2 (vol%)	Reference
Coal-fired Power (UK/EU)	Coal	12–15%	[1]
Fuel Oil Combustion	Fuel Oil	10–12%	[2]
Natural Gas Combined Cycle	Natural Gas	3–5%	[3]
Waste-to-Energy	Municipal Solid Waste	6–10%	[4]
Biogas CHP Plant (Germany)	Biogas	5–7%	[5]
Biomass Combustion	Biomass (Woodchips, Pellets)	10–15%	[6]
Petrochemical Refinery	Mixed Hydrocarbons	8–10%	[7]

On the other hand, in the pursue of the Net Zero emissions ambition, CCUS is expected to grow in the years to come, and therefore it is required to monitor carbon dioxide emissions from post combustion capture plants. Given the current efficiency of the post combustion capture process, the expected CO_2 concentration in the PCC flue gas is expected to be around or below 1%, and as the capture technology improves, we need to be ready to measure lower carbon dioxide concentrations from PCC stacks. It is worth mentioning that the direct monitoring emissions from those facilities is required since any rough estimation of the emissions based on mass balances will produce data with uncertainties larger than those required to actually make valuable quantitative evaluations of these reduced emissions.

This works present some preliminary findings on the use of commercially available devices based on FTIR and Mid IR spectrometry, to measure simulated carbon dioxide emissions in the range of 0.01 to 1% in volumetric concentration.

2 Equipment specifications

Table 1. Equipment used and their associated uncertainties.

Technique	Equipment	Measurement range	Measurement uncertainty
FTIR	Gasmet DX4000 FTIR gas analyser	ppm to 20% vol	10-15%
Mid IR spectrometry	Aeris Technologies MIRA Ultra N_2O/CO_2 analyser	ppm to 100%	>10ppm ~2%

The uncertainty values used within this report are considered the worst case scenario, so that 15% uncertainty is attributed to FTIR results and 2% is assumed for Aeris measurement values. Also, the double of the standard deviations from the average value were used to illustrate the stability of the measurements.

3 Test set up

The stack simulator was rigged so that gas could be piped from gas cylinders of known concentrations of carbon dioxide, oxygen, nitrogen and water vapour, in addition to waste gas mixtures were plumbed into the simulator to generate a flow rate of approximately 105 L/min to simulate typical flue gas mixtures expected within PCC stacks. This flue gas mixture was then split, with it being fed through a gas conditioner to remove moisture and then into the Aeris, into the FTIR, with the remaining being vented to atmosphere, as illustrated in Figure 1.

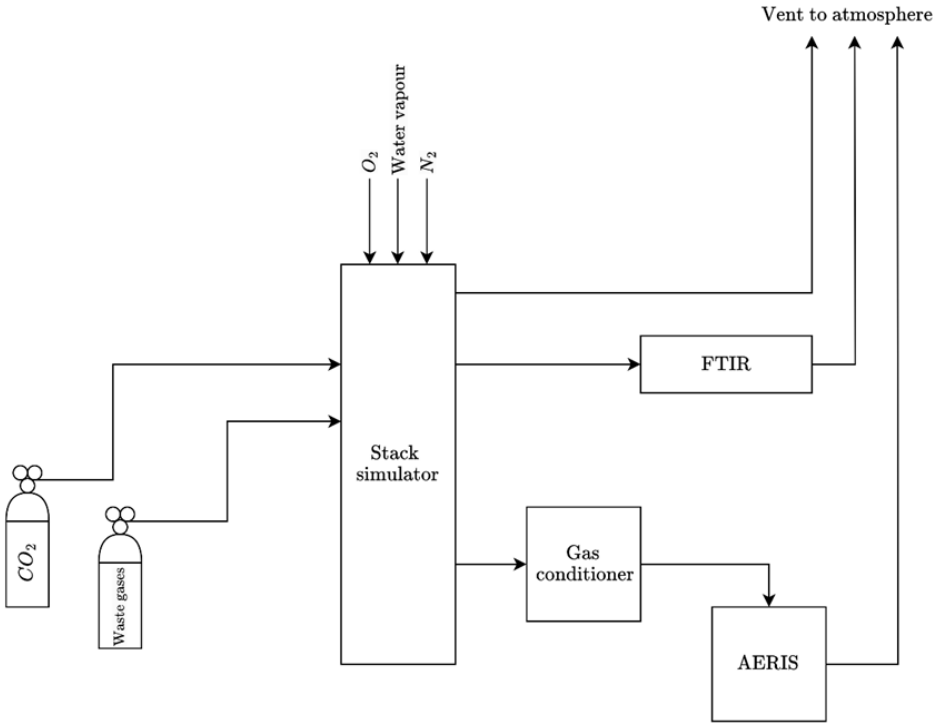

Figure 1. Schematic of the testing set up in the stack simulator

There are available techniques for measuring carbon dioxide in standard operational conditions in different kind of plant's stacks. However, in the context of the Carbon Capture industry, it is still necessary to assess the capability of such technologies to measure relatively low concentrations of CO_2 in stack conditions. Since most reports indicate that the post capture gas has CO_2 concentrations in the range of few units' percent (in volume) or even below, the present report is focused on carbon dioxide concentrations below 1% (equivalent to 10000 ppm or µmol/mol).

Flue gas concentrations of nominally 100, 1000, 5000 and 10000 ppm were simulated, with both dry and wet mixtures also assessed. For target concentrations of CO_2 between 100 to 1000 ppm were generated by a 12% CO_2 certified cylinder with flow rates of between 0.4-2 L/min, while target concentrations above 1000 ppm to 10000 ppm were generated by the use of 100% CO_2 gas cylinder at flow rates of 0.5-2 L/min. One test series of both wet conditions and with the addition of other waste gases (carbon monoxide, NOx, hydrogen chloride and ammonia) which would be present within PCC flue gas was assessed as the closest analogue to what would be encountered in the field.

The concentration ranges for CO_2 and the concentration of water vapour and additional waste gas species were selected from the output of previous projects within both MetCCUS (A2.1.1) and further NPL projects focusing on carbon capture and carbon capture technologies, collating the ranges of the gas species reported from historic and present-day PCC plants.

Table 2. Concentration ranges of key pollutants emitted from PCC plants.

Species	Minimum concentration	Maximum concentration	Mean concentration
CO_2 % vol	3.6	17.8	12.2
H_2O % vol	2.5	18.2	10.5
SO_2 ppm	0.75	230.0	49.6
NOx ppm	3	133.0	68.0
O_2 % vol	3.2	14.0	7.8

However, there are other references showing even lower CO_2 post capture emission values, as the reported < 1.5 vol% residual CO_2 (up to 99.7% capture) achieved in the Waste-to-Energy CHP pilot plant (Edinburgh) which burnt waste for energy and capture the carbon dioxide using MEA at 35% as scrubber solution [8].

The Aeris responded as was anticipated from the previous performance characteristics assessment within A2.2.6 with fast response times. At a target concentration of 100 ppm, the Aeris reported 12% more than the actual CO_2 concentration, while the FTIR reported more than twice, both values falls well outside the measurement uncertainty for both devices (Figure 2). Above 100 ppm (1000, 5000 and 10000 ppm), although the FTIR consistently reports higher concentrations than the Aeris, these values are within the nominal uncertainty of 15% (Figure 3), although the Aeris instrument exhibits more stable readings along the time.

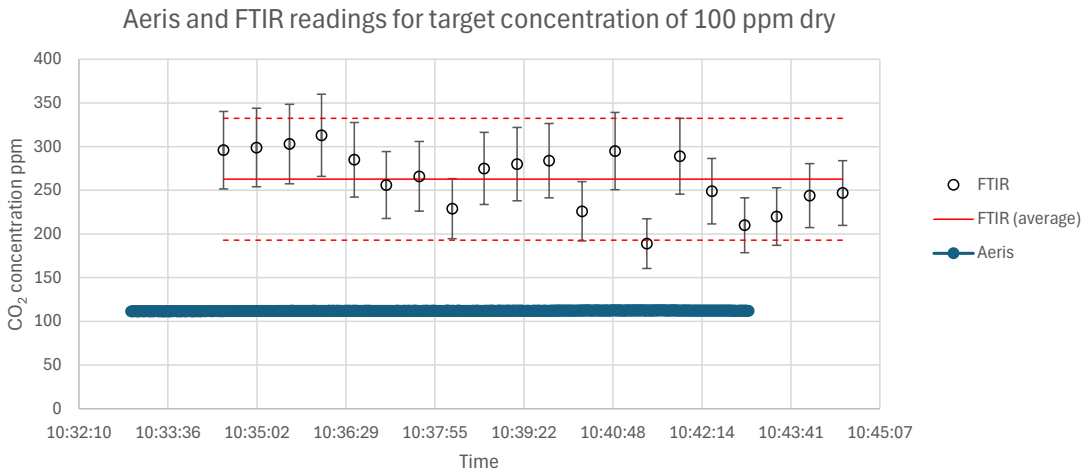

Figure 2. Aeris and FTIR concentration readings for target concentration of 100 ppm CO_2 in a dry gas matrix. Dashed red lines correspond to the expanded uncertainty (2σ).

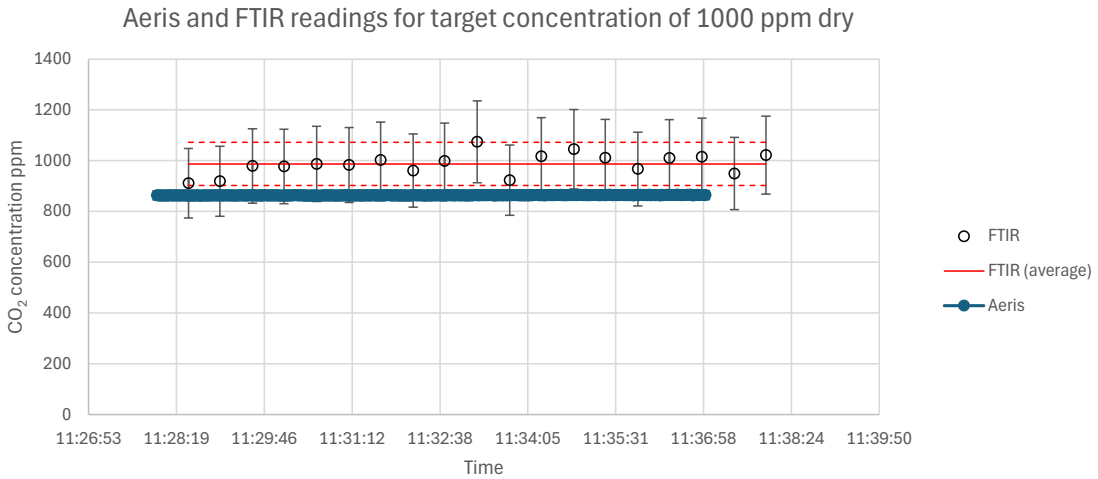

Figure 3. Aeris and FTIR concentration readings for target concentration of 1000 ppm CO_2 in a dry gas matrix. Dashed red lines correspond to the expanded uncertainty (2σ).

The Aeris reported CO_2 accurate values for concentrations ≥ 5000 ppm, showing deviations lower than 4%. However, for lower concentrations there are significant departures from the nominal value, 14% below for 1000 ppm and 12% above for 100 ppm, although the stability of the measurements is always better than 1%. On the other hand, the used FTIR equipment consistently over reported values, with the largest percentage difference

occurring at a target concentration of 100 ppm where the FTIR reported more than twice the nominal value and showed an additional 5 to 50% over measurement even for the higher measured concentrations.

The moisture content of the flue gas matrix did not seem to have a large impact on the FTIR reported measurements. However, the Aeris did report reading closer to the target concentrations in wet gas matrices when compared to the dry gas mixtures (Figure 4). No discernible influence in concentration measurements was seen with the addition of additional waste gas mixtures to the flue gas matrix (Figure 4).

Table 3. Wet and dry gas concentration readings for the Aeris and FTIR for the target CO_2 concentrations within the stack simulator.

Test No.	Wet or Dry	CO_2 Target Concentration Ppm	Aeris CO_2 Average Ppm	Aeris 2σ ppm	FTIR CO_2 Average ppm	FTIR 2σ ppm
2	Dry	100	112	1	260	73
3	Dry	1000	863	2	990	85
4	Dry	5000	4820	19	5250	81
5	Dry	10000	9650	41	10940	100
6	Wet	10000	9990	25	10640	81
7	Wet + waste gases	10000	10000	28	10740	89

In figure 4 the data from Table 3 is plotted. In order to compare the performance of the two used instruments when exposed to CO_2 concentrations at different orders of magnitude, the readings have been normalised to the nominal (certified) concentration values, to allow a direct comparison within the same plot.

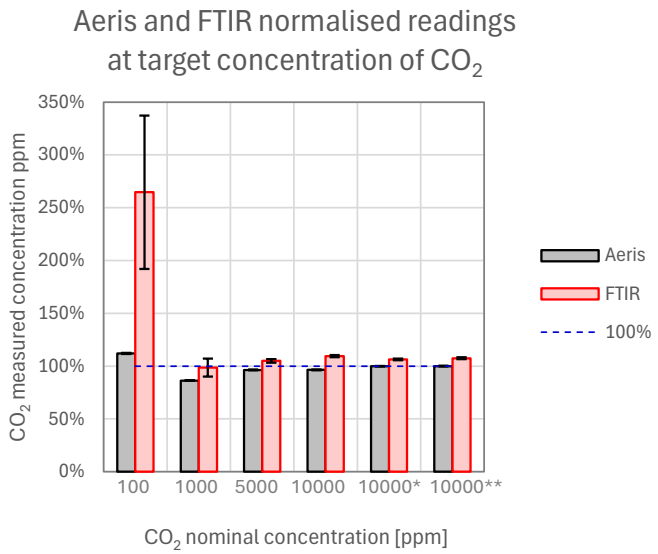

Figure 4. Aeris and FTIR normalised concentrations for target concentration of CO2. Most test were done with dry gas, * wet gas, and ** wet gas and with additional waste gas mixtures. Error bars correspond to 2σ, to show the stability of the readings (these can be seen in the individual test plots).

4 Conclusions

This experimentation has shown that the Aeris works well as a standalone detector to analyse CO_2 concentration within flue gas matrices within the range from 100 to 10000 ppm (0.01 to 1% v/v), being in principle suitable for PCC plants CO_2 monitoring. On the other hand, the FTIR can measure reasonably well (within 10%) from 1000 to 10000 ppm but not at 100 ppm. Intermediate measurements are needed to complete this assessment.

The Aeris responds well at the lower concentrations of carbon dioxide anticipated to arise from PCC plants as technologies continue to develop and the efficiency of carbon removal improves. This range of low concentrations is unlike measurable with the current methodologies, which are used to measuring the higher concentrations from traditional combustion plants.

Further work is needed to systematically assess the impact of dry and wet gas mixtures has on the concentration of carbon dioxide when reported by these two detectors, and whether the discrepancies seen within this report are due to interferences within the instrument measurements themselves or if more complex physiochemical reactions are taking place within the stack matrices themselves.

5 References

1 https://assets.publishing.service.gov.uk/media/5a7c6b4be5274a5590059bd1/Comparison_of_Electricity_Conversion_Factors.pdf

2 https://www.forestresearch.gov.uk/tools-and-resources/fthr/biomass-energy-resources/reference-biomass/facts-figures/carbon-emissions-of-different-fuels/

3 https://www.gov.uk/government/publications/greenhouse-gas-reporting-conversion-factors-2025

4 https://link.springer.com/article/10.1007/s10098-021-02049-4

5 https://link.springer.com/chapter/10.1007/978-3-031-29294-1_6

6 https://uk-air.defra.gov.uk/assets/documents/reports/cat11/1708081027_170807_AQEG_Biomass_report.pdf

7 https://link.springer.com/content/pdf/10.1007/s13203-014-0050-5.pdf

8 https://era.ed.ac.uk/bitstream/handle/1842/41688/Su2024.pdf

6 Annex

Table 4. breakdown of maximum, minimum and mean concentrations of key gas species found within PCC plants.

Gas species	Minimum concentration	Maximum concentration	Mean concentration
CO_2 % vol	3.6	17.8	12.2
H_2O % vol	2.5	18.2	10.5
SO_2 ppm	0.75	230.0	49.6
NOx ppm	3	133.0	68.0
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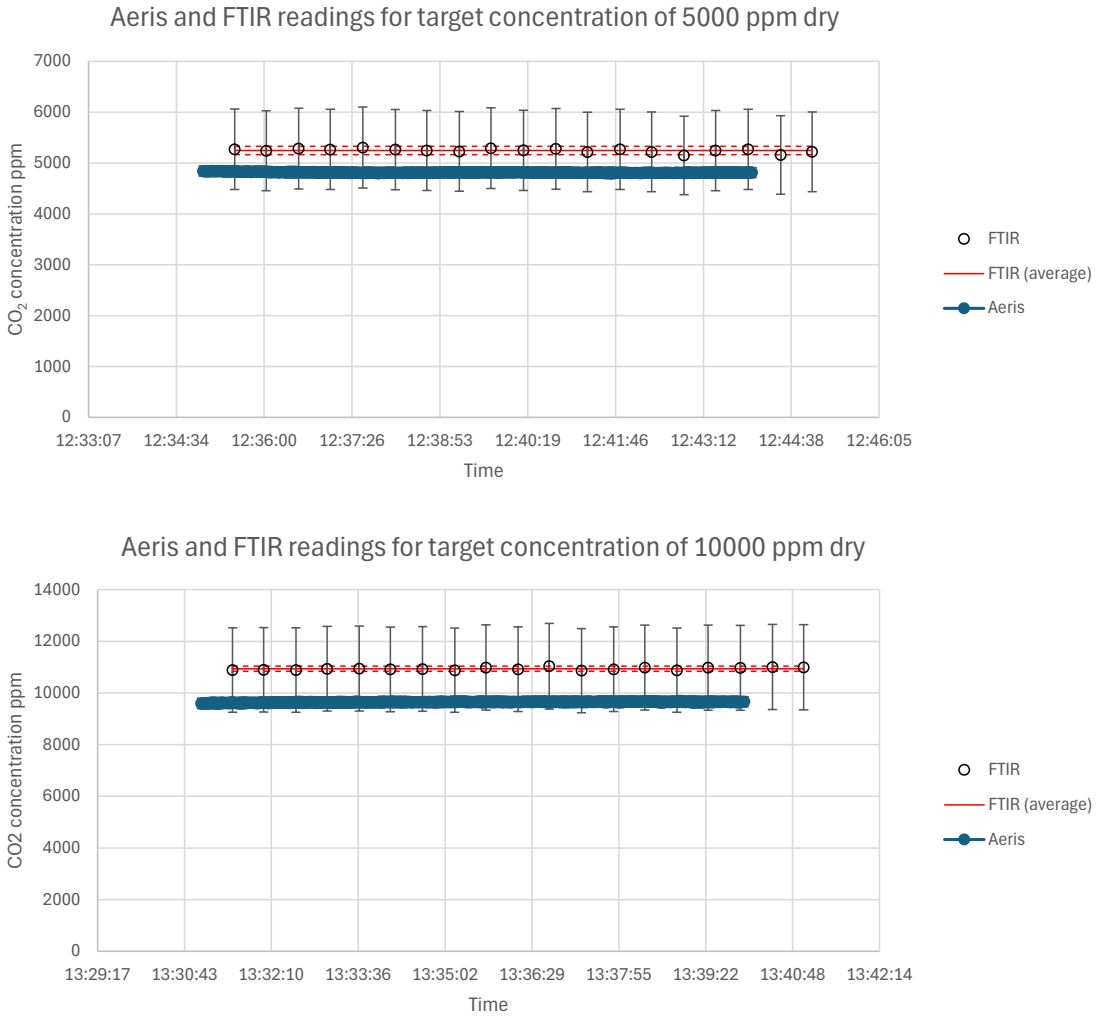

Figure 5. Aeris and FTIR measurements for target concentrations of 5000 and 10000 ppm within a dry flue gas matrix and associated uncertainties.

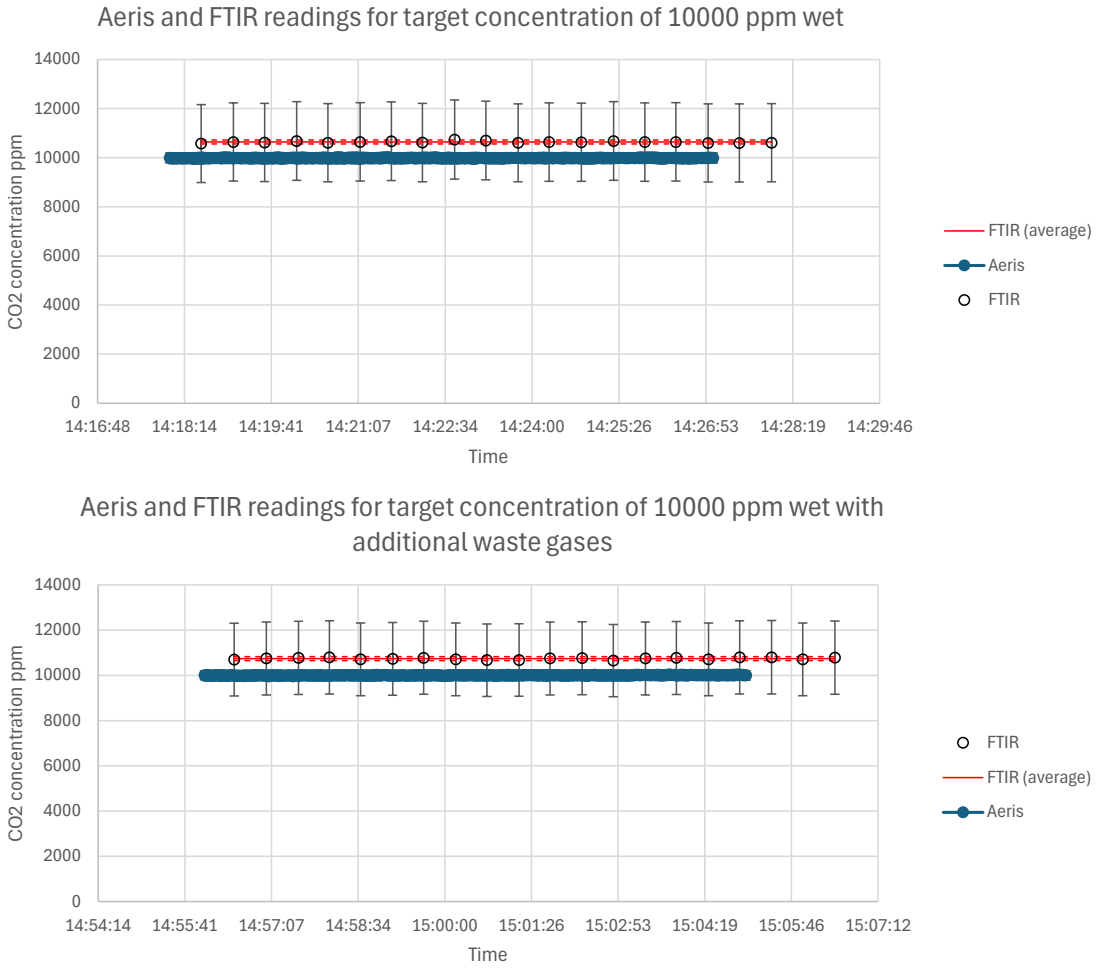

Figure 6. Aeris and FTIR measurement results for a target concentration of 10000 ppm alone and with additional waste gases within a simulated wet flue gas matrix, and associated uncertainties.