SEVENTH FRAMEWORK PROGRAMME

OCTAVIUS

OPTIMISATION OF CO_2 CAPTURE TECHNOLOGY ALLOWING VERIFICATION AND IMPLEMENTATION AT UTILITY SCALE

OCTAVIUS WP12.1 Results : Analysis methodology developed & round robin tests on liquid and gas samples

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Octavius CCS Conference - Rueil-Malmaison - France, 17-19 November 2015

INERIS controlling risks for sustainable development | ifp Energies nouvelles | SINTEF | e·on | Lovelace | RAMBOLL | EPRI ELECTRIC POWER RESEARCH INSTITUTE | EnBW | GASSNOVA | ccsp Carbon Capture and Storage Program

Contents

- Introduction
- Example of emission sampling and analyses of nitrosamines
- Round Robin Tests on Nitrosamines Analysis in the Effluents of a CO_2 Capture Pilot Plant
- Conclusions

Introduction, Context and Objectives,

- **Processes of post combustion CO_2 capture using amine based solvents likely to generate, and are likely to emit:**
  - **common pollutants like SO_2, NO_x, CO, CO_2, aldehydes, etc**
  - **nitrogenous based compounds including nitrosamines which may be formed as solvent degradation products and whose effects on environment and human health may be of importance.**

- **Potential sources of nitrosamines (INERIS 2014): water treatment (both water treatment for drinking purposes and waste water treatment), rubber production, food processing industry, manufacture of cosmetic products, metal machining (by using cutting fluids).**

- **Work package lead by INERIS within Octavius FP7 project SP1:**
  - **dedicated to providing guidelines, methodologies for measurements of emitted regulated pollutants, amines and degradation products in gas and liquid**
  - **nitrosamines: Limited data available in terms of comparability of results and uncertainties of methods, need for comparison data, round robin tests suitable manner of providing such data.**

INERIS Fiche Substances Nitrosamines, November 2014

Introduction, Context, Objectives,

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- **Compounds and levels of concentration:**
  - **Formation/degradation reaction of unstable compounds happening;**
  - **Some compounds likely to be present at very low levels;**

- **Specificity of the matrices**
  - **flue gas:**
    - High moisture content;
    - Low temperature;

    → saturated flue gas, risk of condensation
  - **water wash and solvent matrices:** amine base matrices make difficult the extractions of aminated compounds

- **Compounds likely to remain stable under the flue gas conditions SO_2, NOx, aldehydes, CO, CO_2: standard methods (or adaptation) for stationary combustion sources can be used;**

- **Compounds not likely to remain stable under the flue gas conditions aminated compounds (amines, nitrosamines, amides, nitramines): main focus**

Example of emission sampling and analyses of nitrosamines

Andreas Grimstvedt, Kolbjørn Zahlsen and Kai Vernstad
SINTEF Materials and Chemistry

Contents

- Sampling
- Analysis
- Quality Control

Emission sampling of Nitrosamines

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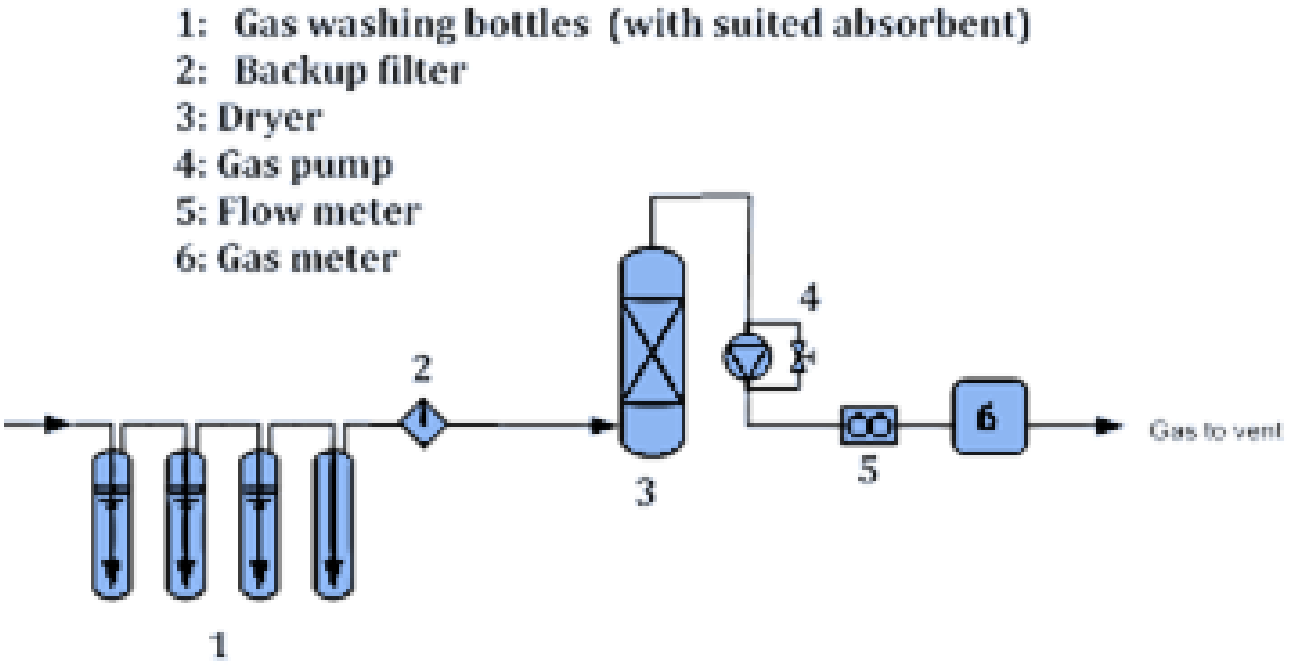
Background

- Dry absorbents like Thermosorb have been widely used for air sampling, however due to the high moisture in amine flue gas they are not suited (get wet)
- H_2SO_4 have traditionally been used as absorbent for emission sampling of NH_3 and has also been adopted for emission sampling of amines.
- However, regarding nitrosamines, artefacts may occur in H_2SO_4 due to nitrosation of amines or compounds with amine functionality in the presence of NOx (also favoured of low pH)
- Sulfamic acid has been found to be a better alternative for sampling of nitrosamines as it inhibits nitrosation.

Sampling train



- Isokinetic
- Gas washing bottles (alternatively impingers)
- Sampling train placed on ice
- Avoid exposure to light

Sampling cont.

- **Heating of sampling line should be used with care, especially when using long lines, as unwanted reactions may occur**
- **Important to avoid contamination and to carefully do the gravimetrically determinations of the absorption solutions (use calibrated balance weight)**
- **Sample should be stored cold if not analysed immediately.**
- **Clear plastic containers are preferred (HDPE etc.)**
- **Blank acid should also be sampled and analysed**
- **Bottles from the same train should not be mixed together but analysed individually (loss of detection capability, QC of efficiency of train)**

Example of analysis of Nitrosamines (EPA mix)

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Pre-treatment

- Absorption solutions (from gas washing bottles/impingers) and condensates are run undiluted, only added internal standards

Calibration standards

- Should be stored cold, some stock solutions are unstable and must be kept frozen
- Some NAs may adsorb to glass containers (like NDMA), plastic is recommended (observed for low conc. < 10 ng/mL NDMA)

Instrumental analysis :
Liquid chromatography with triple quadrupole mass spectrometry (LC-MSMS-QqQ)

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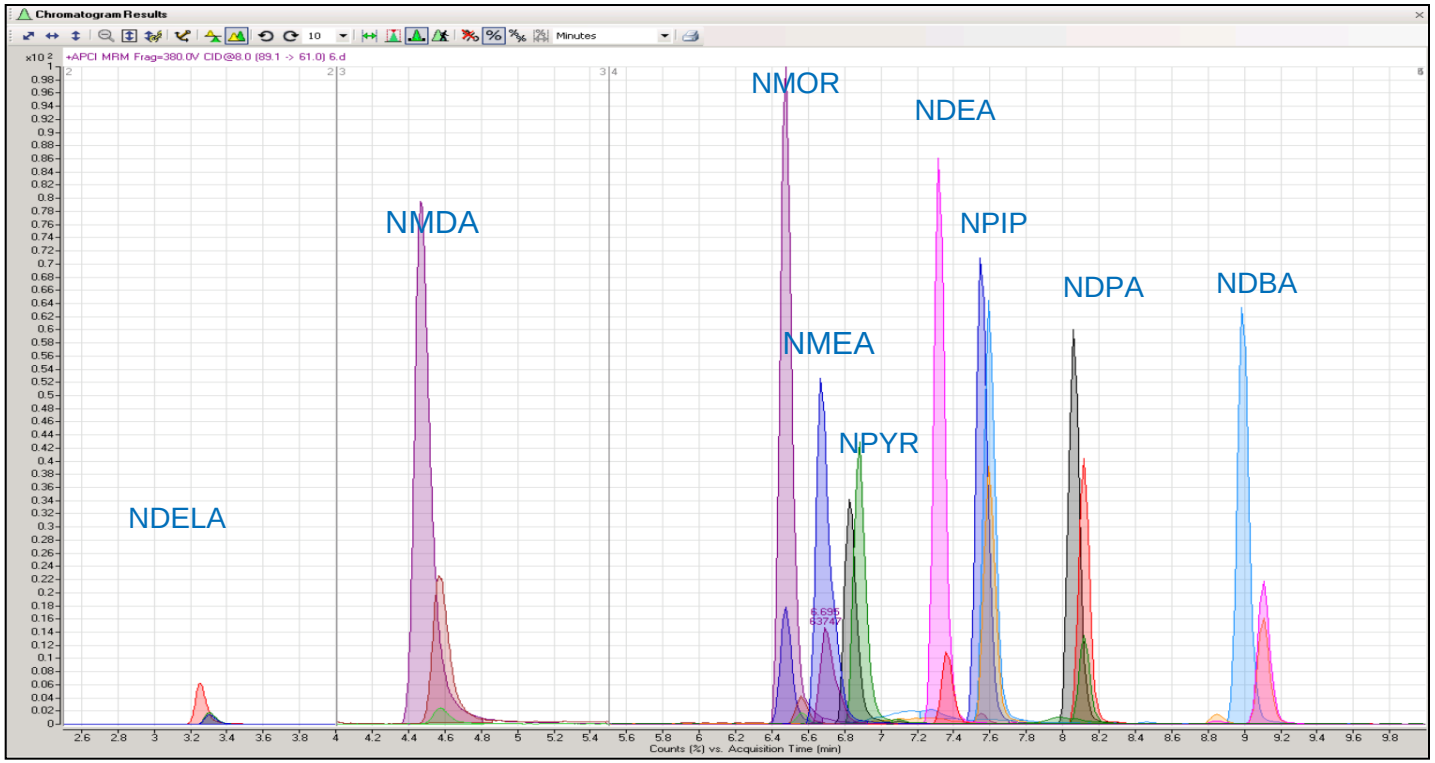
- MS QqQ: Agilent 6490 – (LC-MSMS)
- LC: Agilent 1290
- Column : Ascentis® Express Phenyl-Hexyl, 2.7 Micron HPLC
- Type of Ionisation: APCI (atmospheric pressure chemical ionization)
- Internal standard: Deuterated analogues are used for all analytes (like NDELA-D8, NDMA-D6 etc.)
- Calibration frequencies: 2 calibration curves are run within each analytical series (one before and one after the samples).
- LOQ's: Typical 0,05 – 0,10 ng/mL

Instrumental analyses cont.

Example of chromatogram (standard 10 ng/mL)



Quality Control cont.

- Control of fragmentation pattern (ratio between Quantifier and Qualifier)
- Calibration standards run twice (before and after unknowns) within each analytical series
- QC standard run within each analytical series
- Participation in Round Robin tests
  - Very important tool to independently control the accuracy!!

Sampling

- Control of acid blank used for sampling
- Control of concentration ratios of compounds between bottle 1 and 2
  - In general >90% of the analytes should be absorbed in the first flask.

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Round Robin Tests on Nitrosamines Analysis in the Effluents of a CO_2 Capture Pilot Plant

I. Fraboulet, L. Chahen , F. Lestremau, A. Grimstvedt, B. Schallert, B.C. Moeller, E. Järvinen

Principle of round robin tests (1/2)

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- **To provide to several laboratories homogeneous samples for analyses of targeted species in a specific matrix (original or spiked samples) and compared results obtained.**

- **The aim of round robin tests is to evaluate the capability of measurement methods to provide accurate and reliable results.**

- **Two round robins performed within Octavius:**
  - **on solvent samples, organised by IFPEN**
  - **on atmospheric emission samples collected in sulfamic acid solution, organised by INERIS**

- **Anonymous results dissemination**

Principle of round robin tests (2/2)

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- **9 Nitrosamines:**

Name
N-Nitrosodimethylamine (NDMA)
N-Nitrosomorpholine (NMOR)
N-Nitrosopyrrolidine (NPYR)
N-Nitrosomethylethylamine (NMEA)
N- Nitrosodiethylamine (NDEA)
N-Nitrosopiperidine (NPIP)
N-Nitrosodibutylamine (NDBA)
N-nitrosodipropylamine (NDPA)
N-Nitrosodiéthanolamine (NDELA)

- **Homogeneous samples: Sampling transport conditions adapted to instability of nitrosamines, protected from UV light and placed in an ice box (temperature monitoring for the atmospheric emissions samples)**

- **Large diversity of methods and disposals from one lab to another :**
  - **With or without pre-treatment;**
  - **GC or LC separation,**
  - **TEA or MS/MS detection**

➔ **Improves the reliability of the cross-checking**

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Round Robin test on atmospheric samples

Round Robin test on atmospheric emissions matrix

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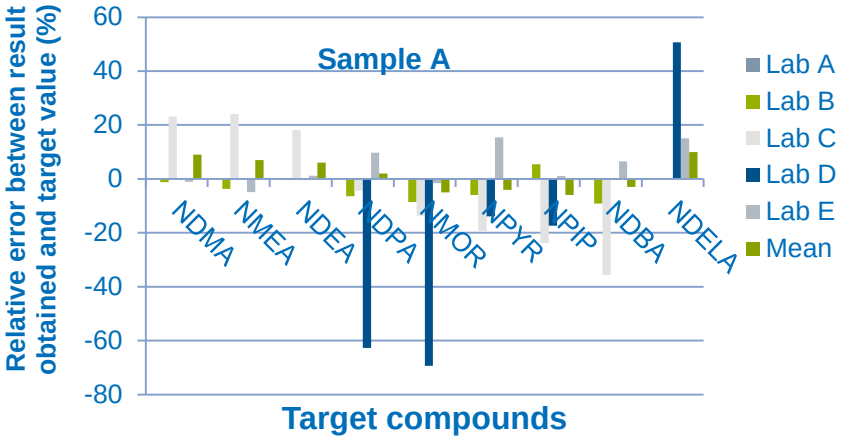
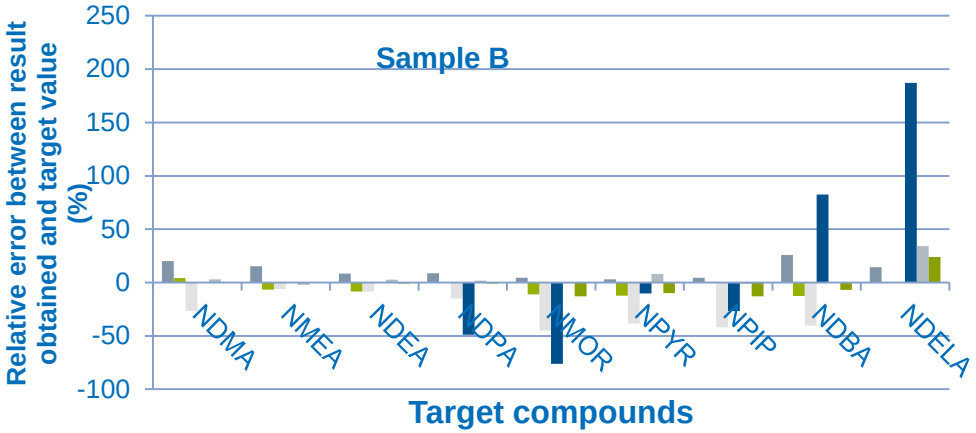
- **Organized by INERIS, 5 participating labs: E.ON (analysis by ISCONLAB, Heidelberg), LRRI, INERIS, RAMBOLL and SINTEF with 5 different analytical methods**
- **Pilot plant duct emissions samples collected during the EnBW campaign, using sampling previously described by SINTEF**
- **Second impingers used as a matrix for spiking**

Compound	SAMPLE A > 1 ng/ml	SAMPLE B < 1 ng/ml
NDMA	6.27	0.44
NMEA	6.31	0.44
NDEA	6.42	0.45
NDPA	6.47	0.45
NMOR	6.50	0.45
NPYR	6.50	0.46
NPIP	6.54	0.46
NDBA	6.48	0.45
NDELA	6.52	0.45

SINTEF 2010 a H&E TQP ID1: Establish sampling and analytical procedures for potentially harmful components post combustion amine based CO2 capture, - Subtask 2 procedure for manual sampling, FM07-AJZ00-S-RA-0001-03, http://www.gassnova.no/no/Documents/Pr

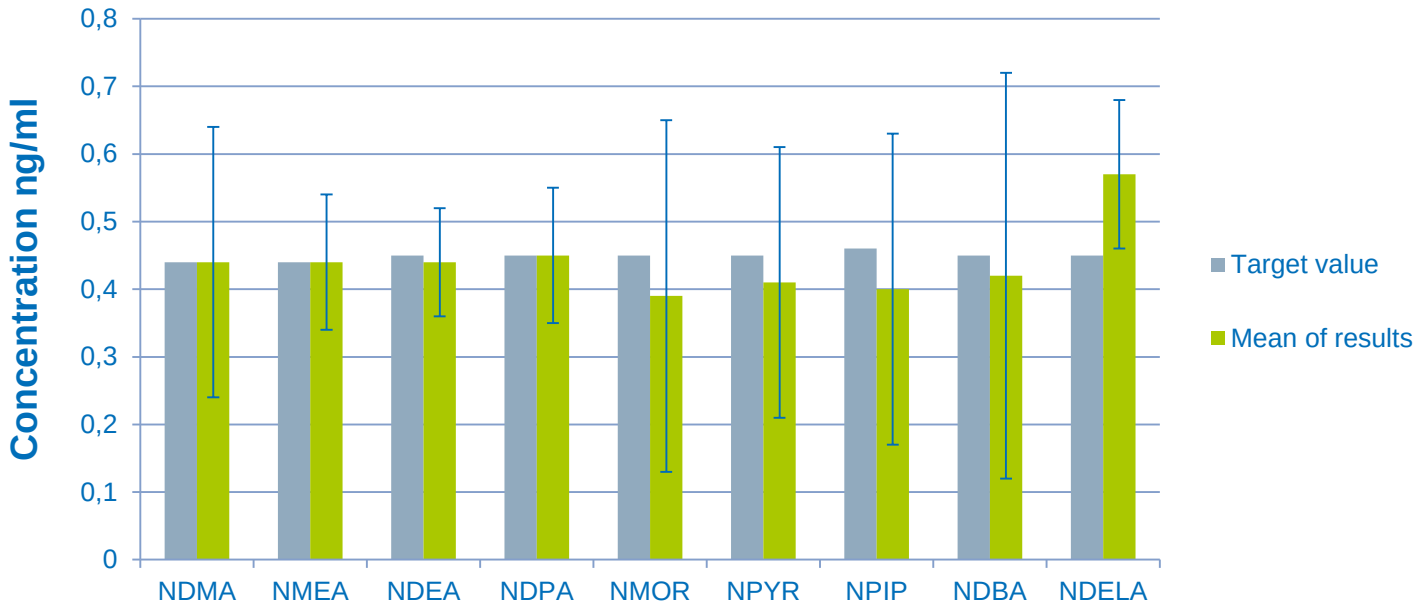
Results: round robin on atmospheric emissions samples, specific nitrosamines





- **Dispersion of relative errors : Sample B > Sample A typical trend for analytical methods generally less precise and accurate at low concentrations compared to high concentrations.**
- **High relative errors been obtained by lab D for NDPA, NMOR, and NDELA:**
  - **NDPA, NMOR due temperature exposure above 25°C samples blocked 10 days during transport,**
  - **NDELA: pre-treatment used by lab D? further investigation necessary.**
- **Results (lab D for NDPA, NMOR, and NDELA) not taken into account into average and standard deviation determination**

Results: round robin on atmospheric emissions samples, specific nitrosamines



- Very good agreement between target value and mean of results
- SD % < 30 %

Methods tested (except method lab D for NDPA, NMOR, and NDELA) appear suitable for the target compounds and range in the studied matrix, analysis of specific nitrosamines from CCS flue gas collected in sulfamic acid well mastered by the participants.

Round Robin test on solvents

Round Robin test on solvents

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- **Organized by IFPEN, 5 labs concerned : E.ON (analysis by ISCONLAB, Heidelberg), IFPEN, INERIS, RAMBOLL and SINTEF**
- **1st step : All partners analyzed 5 blind samples of reference with certified amounts of nitrosamines**
  - **Spiked Samples**
    - **Weighed nitrosamines in MEA 30 wt% loaded at 20 mol% with CO_2**
    - **Concentrations from 0,8 ppb to 1200 ppb**
  - **To check the accuracy of each method**
    - **To allow eventual methods improvements**
    - **To select the most accurate methods for the 2nd step**
- **2nd step : All partners analyzed 6 real degraded solvents from Heilbronn pilot plant**
  - **Real samples from 5 to 1200 hours of operation**
  - **Only the most accurate methods have been considered for final results**
- **Bonus analysis : 2 labs are able to make total nitrosamines analysis and one lab is able to quantify N-Hegly**

Results on synthetic samples

- **Levels quantified: all the nitrosamines quantified up to 1 µg/kg by at least one laboratory, apart from NDELA (43 µg/kg).**
- **Average Relative error**
  - **<10% for 7 nitrosamines : excellent**
  - **19 % for NDELA : acceptable**
  - **38% for NDMA : problem due to contamination of MEA solution**

Compound	Lowest level quantified (µg/kg)	Average relative error
NDMA	-	38%
NMOR	0.9	-6%
NPYR	0.9	-3%
NMEA	0.9	-4%
NDEA	0.9	-8%
NPIP	0.9	-9%
NDPA	0.8	-4%
NDBA	0.9	7%
NDELA	43	19%

Very encouraging results, all nitrosamines can be analyzed with high accuracy by 2 labs at least ➔ confidence for real samples analysis

Results on synthetic samples, Total nitrosamines

	mg of N-NO/kg of synthetic sample Sum of weighed nitrosamines	LAB 1 mg of N-NO/kg of synthetic sample	LAB 2 mg of N-NO/kg of synthetic sample
Sample A	0.11	1.0	1.4
Sample B	0.26	1.2	1.3
Sample C	1.19	2.1	1.8
Sample D	0.04	1.1	1.1
Sample E	0.12	1.1	1.5

- **Results of the 2 laboratories very similar, but largely higher than the sum of the weighed nitrosamines according to the certificate.**
  - **Hypothesis 1 : synthetic solution contain other contaminations than NDMA**
    - **not very likely because, resulting concentrations would have a minor influence compared to those of the weighed nitrosamines.**
  - **Hypothesis 2 : the total nitrosamines analytical methods used by the two laboratories overestimate the amount present in the solution.**
- **Further work necessary on the analysis of total nitrosamines to close the gap between analytical results and target values.**

Results on real samples

- **NPYR, NDEA, NPIP, NDPA and NDBA below LOQ of all labs**
- **Only one laboratory able to quantify the trace level of NDMA, NMOR and the NMEA present at concentrations of few tens of ng/kg in solvent.**
- **NDELA was quantified at higher concentrations by three laboratories, results quite reliable, SD below 20%**

NDELA (µg/kg)	Lab A	Lab C	Lab E	Average	Standard deviation in %
Real sample 1	41	48	60	50	19
Real sample 2	569	660	600	610	8
Real sample 3	470	480	460	470	2
Real sample 4	486	480	510	492	3
Real sample 5	340	370	340	350	5
Real sample 6	323	280	310	304	7

- **N-HeGly also analyzed by one lab, no cross-checking possible**
  - **around 5000 ng/ml in real samples**
  - **< 50 ng/mL in the synthetic samples**
  - **N-HeGly is certainly on of major nitrosamine in the real samples.**

Conclusion concerning round robin tests

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Solvents analysis:

- Nitrosamines methods generally reliable at low concentrations (few ppb) for NDMA, NMOR, NMEA, NPYR, NDEA, NPIP, NDPA and NDBA
- Efforts must be done on
  - NDELA quantification : improve LOQ and accuracy
  - N-HeGly quantification since it may one of the most present nitrosamines
  - Total nitrosamines analysis : interesting method which has to be improved

Atmospheric samples analysis:

- Possible sample degradation due to exposure to high temperature observed
- Globally good results obtained for high and low concentration samples by all laboratories
- Results more dispersed at low concentrations: typical trend of analytical methods generally less precise and accurate at low concentrations compared to high concentrations.
- All methods tested appear suitable for the target compounds and range in the studied matrix.

General Conclusion concerning round robin tests

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- **Round robin is very useful**
  - To improve analytical methods of each participant
  - To be confident on the results on real samples
  - To find consensus on analytical critical points
- **Globally very positive results taking into account the diversity of methods used**
- **Round robin on gas samples globally leads to less dispersed results than on solvant samples, expected result according to differences in matrix characteristics**
- **Feedback concerning round robin organisation:**
  - Temperature monitoring usefull to track high temperature exposure responsible for Nitrosamine lack of stability
  - Risk of contamination, to be adressed by sending blanks solutions together with the samples
  - Results obtained globally validate the organisation process

WP 12.1 Conclusions and perspectives

OCTAVIUS WP12.1 : Analysis methodology developed & round robin tests on liquid and gas samples, main conclusions

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- **Stable compounds monitoring : Existing standardized methods to be used**

- **Nitrosamine measurements:**
  - **Sampling: Recommended sampling train using probe (flue gas temperature, isokinetical sampling) combined with three cold impingers filled in sulfamic acid (as propsed by SINTEF)**

  - **Analysis:**
    - **Extra care to be taken (storage, sample preparation) due to lack of stability of nitrosamines;**
    - **Globally very positive comparison results taking into account the diversity of methods tested during the Octavius project;**
    - **Round robin on gas samples globally leads to less dispersed results than on solvant samples, expected result according to differences in matrix characteristics;**
    - **Total nitrosamines analysis for solvent : interesting method which has to be improved to close the gap with specific nitrosamines.**

Dissemination

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- **Poster at the GHGT 12 conference Austin Texas in 2014 and associated publication in Energy procedia (Volume 63, Pages 1-8134 (2014))**

  "Octavius: Establishment of Guidelines and Standard Operating Procedures (SOPs) Regarding Sampling and Analyses for the Monitoring of Pollutants Emitted in CCS Process Liquid and Atmospheric Matrices"

- **Oral presentation at the TCCS-8 Conference in Trondheim Norway in 2015 and associated publication in Energy procedia (on going) "Round Robin tests on nitrosamines analysis in the effluents of a CO2 capture pilot plant"**

Acknowledgements

The OCTAVIUS Project is supported by the European Commission (Grant Agreement n° 295645).

We also gratefully acknowledge:

- **EPRI and Gassnova who recommended respectively Lovelace Research Institute and Ramboll for participation to the round robins,**
- **ENBW for providing the samples/ matrices from Heilbronn pilot plant,**
- **Octavius partners who provided feedback on measurements**

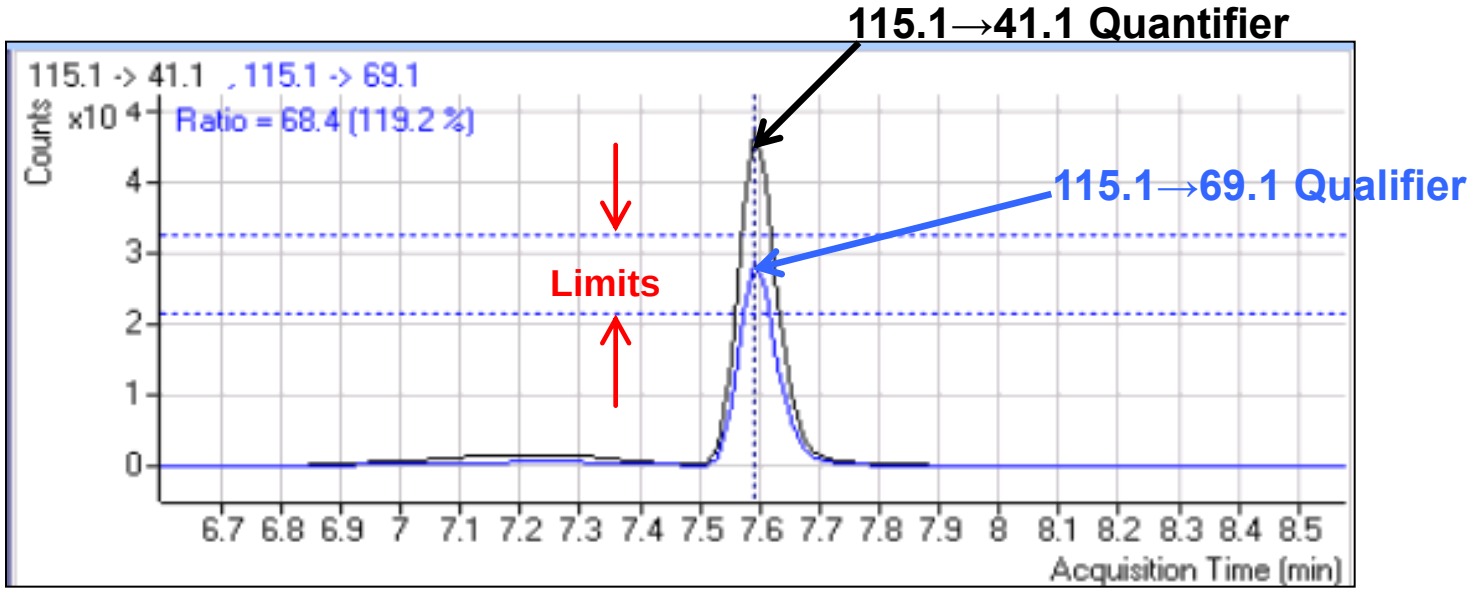
Ramboll ackowldeges the Finnish Carbon Capture and Storage R&D Program CCSP for its additional support.

Quality control

Control of fragmentation pattern (ion ratios)

Example NPIP (N-Nitrosopiperidine), M_W=114,15 g/mol

- **Target m/z = 115,1 $(M+H)^+$**



- Patterns determined for reference standard
- Controlled in samples
- Accepted when qualifier between dashed lines
- Retention time also control criteria

Sample treatments and analytical methods

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Name	Lab A	Lab B	Lab C	Lab D	Lab E
NDMA	LC-MS-MS(QQQ) No pretreatment just diluted sample	GC-MS/MS (SPE)	GC-TEA (LLE)	GC-HRMS (SPE)	GC-HRMS (LLE)
NMOR			GC-TEA (LLE)	GC-HRMS (SPE)	
NPYR			-	-	
NMEA			-	-	
NDEA			-	-	
NPIP			-	-	
NDBA			-	-	
NDPA			-	-	
NDELA		-	GC-TEA Cation exchange and derivatization	LC-MS (SPE)	UPLC-MS/MS (CLLE)
Total nitrosamines	treatment with CuCl and HCl, detection of NO release using TEA		treatment with HBr/Glacial acetic acid/Ethyl acetate and boiling of the mixture at 80 °C, detection of NO		

- **Large diversity of methods and disposals ➔ Improves the reliability of the cross-checking**

Sample treatment and analytical methods, gas emissions samples round robin

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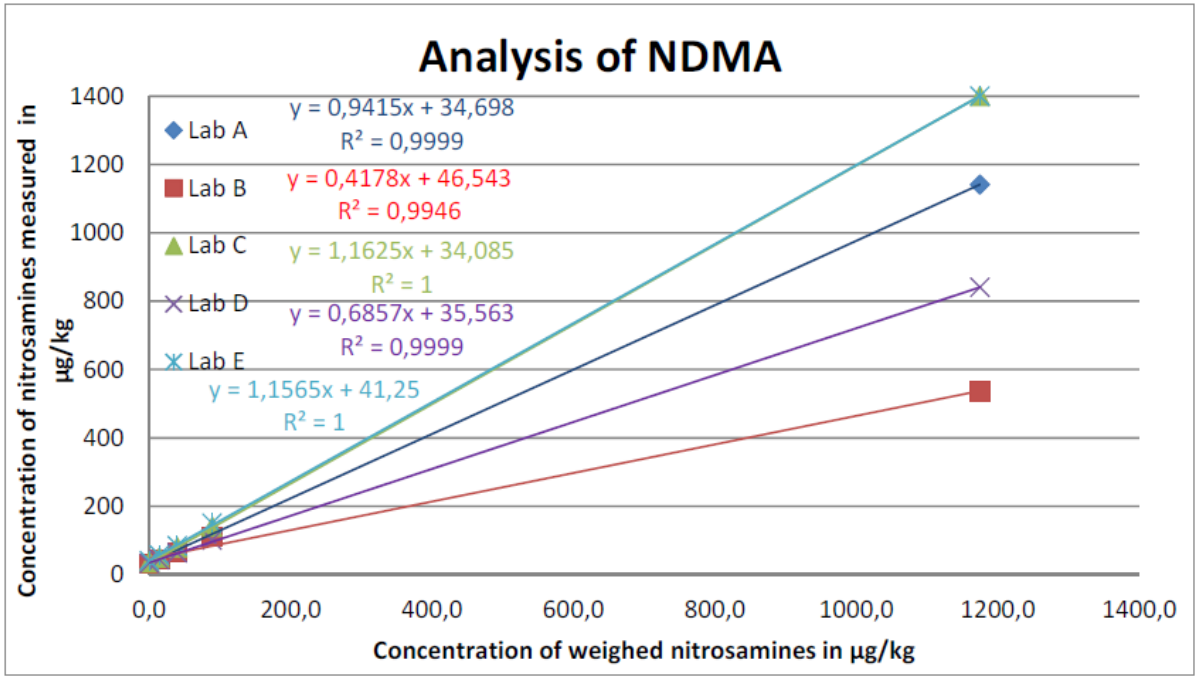
Name	Lab A	Lab B	Lab C	Lab D	Lab E
NDMA	LC-MS-MS(QQQ) No pretreatment just diluted sample	GC-MS/MS (SPE)	GC-TEA (LLE)		GC-HRMS (LLE)
NMOR			GC-TEA (LLE)		
NPYR			-	-	
NMEA			-	LC-MS/MS LLE of 20 mL of sample with 20 mL DCM – concentrated to 0.5 mL of DCM	
NDEA			-		
NPIP			-		
NDBA			-		
NDPA			-		
NDELA		-	GC-TEA Cation exchange and derivatization		UPLC-MS/MS (CLLE)

Specific case of NDMA

- For an accurate method
  - Slope is close to 1
  - Offset close to 0
- Poor slopes mainly due to the point at 1200 ppb which is not realistic
  - Accuracy error <20% at low concentrations for all labs ➔ acceptable



- NDMA : offset of about 35 µg/kg for all labs
  - Contamination of fresh MEA used by NDMA (DMA known to be a side product in the synthesis of MEA)
  - Relative errors observed are not due to the analytical methods
  - For future work, insert a fresh MEA sample in order to trace risk of contamination
- For NDMA in real samples, the results of all labs have been considered