SEVENTH FRAMEWORK PROGRAMME

OCTAVIUS

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

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

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

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# Introduction, context and objectives

# 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 potability purposes and wastewater treatment), rubber production, food processing industry, manufacture of cosmetic products, metal machining (by using cutting fluids).**
- **Specific issues and challenges associated to nitrosamines and CCS matrices (solvent, wash water, atmospheric emissions) :**
  - **Nitrosamines: unstable compounds, very sensitive to UV light exposure, low levels.**
  - **Atmospheric emissions: saturated flue gas.**
  - **Amine based solvent matrix: sample extraction complicated.**

*INERIS Fiche Substances Nitrosamines, November 2014*

# Introduction, Context, Objectives,

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- **Experiences from previous related studies such as the CASTOR and CESAR :**
  - **results from CCS emission measurements quite sensitive to the applied procedures of determination.**
  - **critical to measure these compounds using reliable and accurate methodologies.**
- **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**
  - **aim : to provide standard operating procedures (SOPs) for the measurement (sampling and analyses) of pollutants in CCS matrices (solvent, wash, water, atmospheric emissions) with a special focus on nitrosamines**
- **One of the main conclusions regarding nitrosamines: Limited data available in terms of comparability of results and uncertainties of methods, need for comparison data, round robin tests are a suitable manner of providing such data.**

*CASTOR CO2, From Capture to Storage, FP6 project, CASTOR $CO_2$, From Capture to Storage, FP6 project*

*CESAR $CO_2$ Enhanced Separation and Recovery, FP7 project*

# Material and method

# Material and method: Principle of round robin tests

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- **Principle of a round robin: 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**
- **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)**

# Round Robin test on solvents

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- **Organized by IFPEN, 5 participating labs : E.ON (analysis by ISCONLAB, Heidelberg), IFPEN, INERIS, RAMBOLL and SINTEF with 5 different analytical methods**

- **All partners analyzed 5 blind samples of reference with certified amounts of nitrosamines to check the accuracy of their methods**
  - **Weighed nitrosamines in MEA 30% loaded at 20% with $CO_2$**

| Concentration (µg/kg) | NDMA | NMOR | NPYR | NMEA | NDEA | NPIP | NDPA | NDBA | NDELA |
|---|---|---|---|---|---|---|---|---|---|
| Sample A | 14.9 | 1.3 | 1.3 | 1.3 | 1.3 | 1.3 | 155.6 | 1.3 | 129.8 |
| Sample B | 89.5 | 75.9 | 75.9 | 75.9 | 75.9 | 75.9 | 0.0 | 75.9 | 65.0 |
| Sample C | 1175.1 | 162.0 | 162.0 | 162.0 | 162.0 | 162.0 | 206.4 | 162.0 | 107.5 |
| Sample D | 0.8 | 0.9 | 0.9 | 0.9 | 0.9 | 0.9 | 0.8 | 0.9 | 43.4 |
| Sample E | 39.8 | 10.8 | 10.8 | 10.8 | 10.8 | 10.8 | 0.0 | 10.8 | 216.0 |

- **All partners analyzed 6 real degraded solvents from Heilbronn pilot plant**

# Sample treatment and analytical methods, solvent 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 (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 | | |

# Round Robin test on atmospheric emissions matrix

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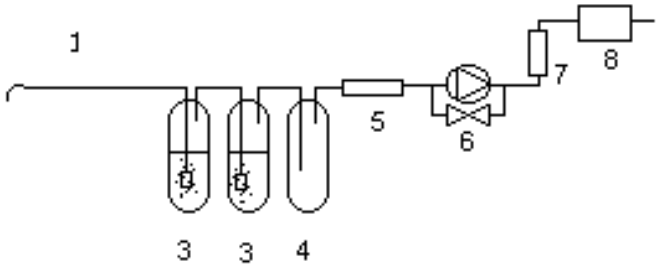
- **Organized by INERIS, 5 participating labs: E.ON (analysis by ISCONLAB, Heidelberg), LRRI, INERIS, RAMBOLL and SINTEF with 5 different analytical methods**
- **Pilot plant duct emissions samples collected during the EnBW campaign**
- **Sampling train used (SINTEF 2010 a) :**




1 :heated sampling probe, isokinetic sampling (glas, teflon)
3 : impingers filled in with 200 ml of 0.1 mol/l sulfamic acid solution placed in an ice bath protected from light with aluminium foil
4: guard bottle (optional)
5: cartridge with desiccant (optional)
6: pump
7: flow meter behind the filter (e.g. diaphragm) or before the gas meter
8: gas meter

- **Second impingers used as a matrix for spiking (concentrations of nitrosamines below LOQ)**

| 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*

# 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) |

# Results

***Nota: For reason of confidentiality, in the rest of presentation, the laboratories will be mentioned by a letter from A to E***

# Results : Analysis of specific nitrosamines in solvent matrices, synthetic samples

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| Compound | Number of labs able to analyse it | Comments | Lowest level quantified (µg/kg) | Max SD(%) | Average relative error | Range of relative error |
|---|---|---|---|---|---|---|
| NDMA | 5 | Possible samples contamination | - | 22% | 38% | from 11% to 67% |
| NMOR | 5 | | 0.9 | 13% | -6% | from-22% to -4% |
| NPYR | 3 | | 0.9 | 14% | -3% | from -12% to 8% |
| NMEA | 3 | | 0.9 | 8% | -4% | from -15% to 8% |
| NDEA | 3 | | 0.9 | 23% | -8% | from -17% to 8% |
| NPIP | 3 | | 0.9 | 32% | -9% | from -26% to 7% |
| NDPA | 3 | | 0.8 | 19% | -4% | from -18% to 9% |
| NDBA | 3 | | 0.9 | 9% | 7% | from 0% to 14 % |
| NDELA | 4 | | 43 | 46% | 19% | from -4% to +41% |

- Lowest standard deviation obtained for NMEA (max SD 8%), highest standard deviation was for NDELA (max SD 46%).
- Relative error: highest obtained for NDMA (38%) and lowest for NPYR (-3%).
- NDMA : offset of about 30 µg/kg observed in the samples. May be due to contamination of fresh MEA used by NDMA. DMA known to be a side product in the synthesis of MEA. Relative errors observed likely not to be due to the analysis of the samples, but to a contamination by traces of NDMA in MEA: For future work, insert a fresh MEA sample in order to trace risk of contamination .
- Levels quantified: all the nitrosamines quantified up to a level of 1 µg/kg by at least one laboratory, apart from NDELA (43 µg/kg).

**Results obtained in different laboratories, using different analytical methods, reliability and accuracy of the methods quite encouraging.**

# Results :Analysis of specific nitrosamines in solvent matrices, real samples

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- 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 of the 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, no cross-checking was possible since was only done by one laboratory. However results (around 5000 ng/ml in real samples and < 50 in the synthetic) for N-HeGly indicate major nitrosamine in the real samples.

# Results: round robin on solvant synthetic samples, total nitrosamines

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| | 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 |
| Relative error in % | Sample A | 833 | 1217 |
| | Sample B | 366 | 416 |
| | Sample C | 76 | 53 |
| | Sample D | 2836 | 2892 |
| | Sample E | 813 | 1140 |

- **Results of the 2 laboratories very similar, but higher than the sum of the weighed nitrosamines according to the certificate. Reasons?**
  - **synthetic solution contain nitrosamines not intentionally introduced and not mentioned in the certificate joined, not very likely because, resulting concentrations would have a minor influence compared to those of the weighed nitrosamines.**
  - **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: round robin on atmospheric emissions samples, specific nitrosamines

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| | Relative error % | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | SAMPLE A > 1ng/ml | | | | | | SAMPLE B < 1 ng/ml | | | | | |
| | Lab A | Lab B | Lab C | Lab D | Lab E | Mean | Lab A | Lab B | Lab C | Lab D | Lab E | Mean |
| NDMA | 15.3 | -1.2 | 23.1 | NA | -1.1 | 9% | 20.1 | 4.1 | -26.8 | NA | 3,0 | 0% |
| NMEA | 10.9 | -3.7 | 24.1 | NA | -4.9 | 7% | 15.3 | -6.6 | -5.9 | NA | -2,2 | 0% |
| NDEA | 4.5 | -0.4 | 18.2 | NA | 1.2 | 6% | 8.4 | -8.3 | -8.4 | NA | 2,8 | -1% |
| NDPA | 9.8 | -6.4 | -4.4 | -62.7* | 9.7 | 2% | 8.6 | 0.2 | -14.9 | -48.9* | 1,9 | -1% |
| NMOR | 4.9 | -8.5 | -13.7 | -69.4* | -1.6 | -5% | 4.6 | -11.2 | -44.9 | -76.3* | -0,7 | -13% |
| NPYR | 2.2 | -5.9 | -19.2 | -13.9 | 15.4 | -4% | 3.1 | -12.4 | -38.4 | -10.1 | 8,2 | -10% |
| NPIP | 3.3 | 5.4 | -23.8 | -17.4 | 1.0 | -6% | 4.5 | 0.7 | -42.1 | -26.8 | -1,2 | -13% |
| NDBA | 25.5 | -9.1 | -35.6 | -0.1 | 6.5 | -3% | 25.8 | -12.6 | -40.4 | 82.5* | -0,3 | -7% |
| NDELA | 4.4 | NA | NA | 50.7* | 15.1 | 10% | 14.5 | NA | NA | 187.3* | 34,3 | 24% |

- High relative errors been obtained by lab D for NDPA, NMOR, and NDELA, likely to be due temperature exposure above 25°C (according to temperature monitoring into the ice box) because samples blocked 10 days during transport, results not taken into account
- Sample A, relative errors between -36% and +25%,
- Sample B, relative errors are a bit higher since, for all results they vary between -45% and +34%, typical trend for analytical methods which are generally less precise and accurate at low concentrations compared to high concentrations.

# Results: round robin on atmospheric emissions samples, specific nitrosamines

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| | Results ng/mL sample | | | | | |
|---|---|---|---|---|---|---|
| | SAMPLE A > 1ng/ml | | | SAMPLE B < 1 ng/ml | | |
| | Target value | Mean of results | SD(%) | Target value | Mean of results | SD(%) |
| NDMA | 6.3 | 6.8 | 11% | 0.44 | 0.44 | 20% |
| NMEA | 6.3 | 6.7 | 13% | 0.44 | 0.44 | 10% |
| NDEA | 6.4 | 6.8 | 8% | 0.45 | 0.44 | 8% |
| NDPA | 6.5 | 6.6 | 9% | 0.45 | 0.45 | 10% |
| NMOR | 6.5 | 6.2 | 9% | 0.45 | 0.39 | 26% |
| NPYR | 6.5 | 6.2 | 14% | 0.45 | 0.41 | 20% |
| NPIP | 6.5 | 6.1 | 14% | 0.46 | 0.40 | 23% |
| NDBA | 6.5 | 6.3 | 23% | 0.45 | 0.42 | 30% |
| NDELA | 6.5 | 7.2 | 7% | 0.45 | 0.57 | 11% |

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

**All methods tested 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.**

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# Conclusions

# Conclusion on the analysis of solvent matrix samples

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- **Synthetic samples:**
  - Possible contamination of MEA samples by NDMA observed;
  - Globally good results taking into accunt the diversity of analytical methods;
- **Real samples:**
  - most nitrosamines: very low amounts determined, most of the labs not able to quantify the nitrosamines
    - Quantification traces of NDMA, NMOR and the NMEA by Lab B only (no cross-checking), tens of ng/kg
    - NPYR, NDEA, NPIP, NDPA and NDBA below LOQ of all labs
  - NDELA and N-HeGly are the most present nitrosamines detected in real circulating solvent solutions
    - The determination of NDELA is quite reliable
    - No cross-checking was possible on N-HeGly
- Gap observed between results obtained by methods for total nitrosamines, and target values : more work necessary on total nitrosamines analytical method to close the gap

# Conclusion on the analysis of atmospheric matrix samples

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- 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 which are 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.
- Analysis of specific nitrosamines from CCS flue gas collected in sulfamic acid well mastered by the participants

# General Conclusion

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- Round robin on gas samples globally leads to less dispersed results than on solvant samples, expected result according to differences in matrix characteristics
- Globally very positive results taking into account the diversity of methods used
- Feedback concerning round robin organisation:
  - Delay due to samples blocked during transport, may be an issue, temperature montoring usefull to track high temperature exposure
  - Risk of contamination may be an issue, to be adressed by sending blank fresh MEA solutions together with the samples
  - Results obtained globally validate the organisation process

# Acknowledgements

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**We also gratefully acknowledge EPRI and Gassnova who recommended respectively Lovelace Research Institute and Ramboll for participation to the round robins, and ENBW for providing the samples/ matrices from Heilbronn pilot plant**

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

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***Thank you for your attention, any questions?***

[P1]Voir avec François l'utilité de mettre 2 décimales



| NDMA (µg/kg) | Weighted Concentration | Lab A | Lab B | Lab C | Lab D | Lab E |
|---|---|---|---|---|---|---|
| Sample A | 14,9 | 47 | 42 | 49 | 44 | 57 |
| Sample B | 89,5 | 126 | 109 | 140 | 101 | 150 |
| Sample C | 1175,1 | 1141 | 536 | 1400 | 841 | 1400 |
| Sample D | 0,8 | 31 | 32 | 36 | 33 | 41 |
| Sample E | 39,8 | 71 | 66 | 80 | 64 | 85 |
| Relative error in % | Sample A | 213 | 185 | 229 | 195 | 283 |
| | Sample B | 41 | 22 | 56 | 13 | 68 |
| | Sample C | -3 | -54 | 19 | -28 | 19 |
| | Sample D | 3834 | 3848 | 4400 | 4025 | 5025 |
| | Sample E | 80 | 64 | 101 | 61 | 114 |


Samples temperature (°C)
30
25
20
15
10
5
0
-5
16/6
18/6
20/6
22/6
24/6
26/6
28/6
30/6
2/7
4/7
6/7
23/06
Samples sent
to lab A and D
25/06 Lab A
Reception of
samples
04/07 lab D
reception of
samples
samples lab
A
samples Lab
D