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

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**Abstract**

Processes of post combustion $CO_2$ capture using amine based solvents generate nitrogenous compounds. Among these products, carcinogenic nitrosamines are of great concern due the potential impacts on the environment and human health. Trace analysis of nitrosamines in simple matrices such as water is well described in standard methods [1]. However, measuring nitrosamines in $CO_2$ capture processes emissions is much more challenging. Nitrosamines, formed to small concentrations as solvent degradation products, may indeed be present in solvent, wash waters, and atmospheric emissions which are more complicated to monitor. Within the FP7 OCTAVIUS project, 2 international round robins on the analysis of 9 nitrosamines in solvent matrices and the atmospheric emissions, from the EnBW $CO_2$ capture pilot plant in Heilbronn (Germany) were organized. The first round robin test was performed on solvent matrices. The analytical methods of the laboratories involved were compared using synthetic spiked samples and liquid samples obtained from the pilot plant. The second round robin test was performed on atmospheric emissions collected using a sampling train with cold impingers filled in with sulphamic acid in water. Each laboratory was provided with two blind samples of the liquid mixture spiked at different levels of concentrations of nitrosamines.

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*Keywords: Post-combustion processes, nitrosamines analysis, round robin, gas effluent, liquid effluent, MEA*

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## 1. Glossary

LOQ: limit of quantification
SOPs: standard operating procedures
CCS: $CO_2$ capture and storage
GC-TEA: Gas chromatography combined to Thermal Energy Analyser Detector
GC-HRMS: Gas chromatography combined to High resolution Mass spectrometry Detector
GC-MS-MS : Gas chromatography combined to Two Mass spectrometry Detectors used in Tandem
LC-MS-MS: Liquid chromatography combined to Two Mass spectrometry Detectors used in Tandem
LC-MS-MS (QQQ): Liquid chromatography combined to Two Mass spectrometry Detectors used in Tandem with triple quadrupole
UPLC-MS-MS: Ultra performance liquid chromatography combined to Two Mass spectrometry Detectors used in Tandem
DCM: Dichloromethane
LLE: Liquid liquid extraction
CLLE: Continuous liquid liquid extraction
SPE: Solid phase extraction
NDMA : N-nitrosodimethylamine, CAS 62-75-9
NMEA : N-nitrosomethylethylamine CAS 10595-95-6
NDEA : N-nitrosodiethylamine CAS 55-18-5
NDPA : N-nitrosodipropylamine CAS 621-64-7
NMOR : N-nitrosomorpholine CAS 59-89-2
NPYR : N-nitrosopyrrolidine CAS 930-55-2
NPIP : N-nitrosopiperidine CAS 100-75-4
NDBA : N-nitrosodibutylamine CAS 924-16-3
NDELA: N-nitrosodiethanolamine CAS 1116-54-7
N-Hegly : N-nitroso-(2-hydroxyethyl) glycine CAS 80556-89-4

## 2. Introduction

Processes of post combustion $CO_2$ capture using amine based solvents are likely to generate, and emit, not only common pollutants like $SO_2$, $NO_x$, CO, $CO_2$, aldehydes, etc. but also nitrogenous based compounds whose effects on environment and human health may be of importance. Moreover, experiences from previous related studies such as the CASTOR[†] and CESAR[‡] programs have shown that the results from $CO_2$ capture processes emission measurements may be quite sensitive to the applied procedures of determination. As a result, it is critical to measure these compounds using reliable and accurate methodologies. This is particularly true when taking into account the specific issues and challenges associated to matrices (circulating solvent, wash waters, and atmospheric emissions) of $CO_2$ capture using amine based solvent processes and the difficulty of measuring nitrogenous compounds in such matrices. Previously, several research groups studied the degradation products of MonoEthanolAmine (MEA), including nitrosamines analysis [2,3], however they were obtained from measurements performed on different pilot plants with various analytical methods, which makes comparison of results complicated.
Within OCTAVIUS EU FP7 SP1 subproject, a work package has been dedicated to the promotion of guidelines for the measurement of regulated pollutants ($SO_2$, NOx, aldehydes, CO, $CO_2$, etc) and nitrogenous compounds (amines, nitrosamines, amides, etc) in the three matrices generated by $CO_2$ capture processes using amine based solvents i.e atmospheric emissions, wash water liquid wastes and circulating solvent. Its aim was to provide recommendations under the form of standard operating procedures (SOPs), to be used as a common methodology [4].

[†] CASTOR $CO_2$, From Capture to Storage, FP6 project
[‡] $CO_2$ Enhanced Separation and Recovery, FP7 project

Within this work package, round robin tests have been performed on nitrosamine analyses in order to compare the methods used. The proposed paper presents the work done and the results obtained.

## 3. Description of the round robin tests performed

### *3.1. Principle of round robin tests*

The aim of round robin tests was to evaluate the capability of measurement methods to provide accurate and reliable results. It consisted in providing several laboratories homogeneous samples that were analysed and results compared. Two matrices were used to perform round robin tests within the Octavius program:

- A round robin on solvent matrix organized by IFPEN;
- A round robin on atmospheric matrix collected using the sampling train described in Figure 1 organized by INERIS

They have been performed using pilot plot samples or model samples of those two matrices which were split and in some cases spiked with a known amount of a mixture of several nitrosamines. A description of pilot plant samples is presented in Table 1. The target compounds for the round robin are presented in Table 2.

Table 1: Pilot plant samples description

| **Type of sample** | **Sample** ID | **Sampling Date** | **Pilot plant operating hours** |
|---|---|---|---|
| **ENBW MEA 30% Lean Solvant** | Sample 1 | 30.10.2013 | 5 |
| **ENBW MEA 30% Lean Solvant** | Sample 2 | 03.12.2013 | 564 |
| **ENBW MEA 30% Lean Solvant** | Sample 3 | 30.01.2014 | 949 |
| **ENBW MEA 30% Rich Solvant** | Sample 4 | 30.01.2014 | 949 |
| **ENBW MEA 30% Rich Solvant** | Sample 5 | 14.02.2014 | 1173 |
| **ENBW MEA 30% Rich Solvant** | Sample 6 | 19.02.2014 | 1224 |
| **ENBW Gaseous Emission samples** | Samples A and B | 10.02.14 - 14.02.14 | 1072 - 1179 |

Table 2: Nitrosamines in synthetic samples

| Name | Molecular weight (g/mol) | CAS |
|---|---|---|
| **NDMA** | 74,08 | 62-75-9 |
| **NMOR** | 116,12 | 59-89-2 |
| **NPYR** | 100,12 | 930-55-2 |
| **NMEA** | 88,11 | 10595-95-6 |
| **NDEA** | 102,14 | 55-18-5 |
| **NPIP** | 114,15 | 100-75-4 |
| **NDBA** | 130,19 | 924-16-3 |
| **NDPA** | 158,24 | 621-64-7 |
| **NDELA** | 134,13 | 1116-54-7 |

Among these 9 nitrosamines, 7 are known as common pollutants in water analysis (EPA 521). NDELA and NMOR are nitroso-derivatives of suspected degradation products of MEA: diethanolamine and morpholine, respectively.

### *3.2. Laboratories and methods*

Each one of the round robin tests has been organized between 5 different laboratories:

- E.ON, INERIS, IFPEN, SINTEF and RAMBOLL for the solvent samples;
- E.ON, INERIS, EPRI, SINTEF and RAMBOLL for the atmospheric samples collected in sulfamic acid solutions.

For reason of confidentiality, in the rest of the paper, the laboratories will be mentioned by a letter from A to E. After preparation the samples were sent to the participants in glass bottles protected from UV light placed in an ice box. The participants were encouraged to maintain these conditions of storage in their laboratories and to analyse the samples as soon as possible to avoid any evolutions of the samples. The methods used by the participants are presented in Tables 3 and 4.

Table 3 : Methods used during the round robin test on solvent samples

| 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 | | |

Table 4: Methods used during the round robin test on gas samples

| 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) |

Each laboratory developed its own analytical approach either with or without sample pre treatment or concentration steps. This diversity ensures a better confidence in the results of the round robin tests. There is no standard method available for the measurement of nitrosamines in matrices generated by processes of post combustion $CO_2$ capture using amine based solvents. Previous guidelines [5,6] regarding analytical methods to be used for the measurement of nitrosamines have recommended when possible, to avoid extractions, and to prefer dilution or direct injection because it causes minimal interference with the sample and is a very simple and cost-effective way to prepare a large number of samples. However, in order to reach low quantification limits and improve the performance of the method, extraction, cleanup (removal of contaminants) and concentration steps may be necessary. I that case, it must be controlled and verified that no degradation or unwanted chemical reactions take place during the whole sample preparation process and analysis.

### *3.3. Round robin test on solvent samples*

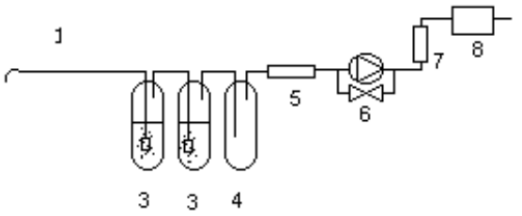
The first round robin test on nitrosamine analysis from MEA (30 wt.%) samples was organized by IFPEN, in which 4 more laboratories participated. IFPEN provided each participant 5 model samples spiked with nitrosamine (Table 2) concentrations ranging from 0.5 ng/mL to 1500 ng/mL and 6 samples collected during a sampling campaign at the EnBW $CO_2$ capture pilot in Heilbronn (Germany). This round robin test was focused on specific and total nitrosamine analyses. The synthetic solutions contained 20% $CO_2$ and had a density of 1.0598 g/cm$^3$. Each partner received 100 mL of each synthetic solution in brown glass that were maintained in the dark at 4-8°C in isotherm boxes during transport. All spiked solutions were prepared by weighing from freshly ordered nitrosamine powders or solutions provided by Sigma-Aldrich. NDMA, NMOR, NDELA and NDPA were purchased individually and all others nitrosamines were purchased as a mixture at 2 mg/mL of each nitrosamine in methanol. The concentrations of nitrosamines in the 5 synthetic solutions are given in Table 5.

Table 5: Concentrations of nitrosamines in synthetic solutions

| 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 |

### *3.4. Round robin test on atmospheric samples from pilot plant emissions collected in sulfamic acid solutions*

A second round robin organized by INERIS, gathered five laboratories that were provided with samples obtained during a sampling campaign performed at the EnBW CCS pilot plant located in Heilbronn (Germany). The samples were taken by collection of flue gas in a solution of sulfamic acid in water using the sampling train described in Figure 1 [7].




**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**

Figure 1: Sampling system used to collect atmospheric emissions

The sampling train was composed of two impingers. In the second impinger, nitrosamines concentrations were below INERIS limits of quantification, as a result these samples were used as a matrix for spiking with a known amount of a mixture of the nitrosamines. They were respectively spiked with 23 µL and 300 µL of a standard solution at 10 µg/mL in methanol to 100 mL of sample (Table 6) resulting in a low (below 1 ng/ml) and a high (above 1ng/ml) level of concentration of nitrosamines.

Table 6: Concentrations of nitrosamines in sulfamic acid in water, spiked, solutions

| 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 |

The samples were stored in glass bottles covered with aluminium foil and kept in a refrigerator (2-8°C) and sent to the participants in an ice box equipped with a data logger for temperature monitoring.

## 4. Results

### *4.1. Analysis of specific nitrosamines in solvent matrices*

A synthesis of the results obtained for analysis of specific nitrosamines in synthetic spiked solvent samples is presented in Table 7.

Table 7: Synthesis of the results obtained for analysis of specific nitrosamines in synthetic spiked samples

| Compound | Number of laboratories able to analyse it | Comments | Lowest level quantified (µg/kg) | Standard deviation | Average relative error | Range of relative error |
|---|---|---|---|---|---|---|
| **NDMA** | 5 | large relative error due to 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% |

Only NDMA and NMOR could be analysed by the five laboratories. The lowest standard deviation was obtained for NMEA with a value below 8%, the highest standard deviation was obtained for NDELA with a value below 46%. In terms of relative error, the highest level was obtained for NDMA with 38% and the lowest for NPYR with -3%. Concerning NDMA an offset of 30 µg/kg was observed in the samples. This offset may be due to the presence of NDMA in MEA. Indeed, dimethylamine (DMA) is known to be a side product in the synthesis of MEA. Thus, it is likely to have traces of NDMA in MEA. The relative errors observed are likely not to be due to the analysis of the samples, but to a contamination from the initial solution. In terms of levels quantified, apart from NDELA for which the lowest level quantified was 43 µg/kg, all the nitrosamines could be quantified up to a level of 1 µg/kg by at least one laboratory.

Taking into account the fact that these results were obtained in different laboratories, using different analytical methods, the reliability and accuracy of the methods is quite encouraging. For future work, it will be interesting to insert a fresh MEA sample (not spiked) in the round robin test in order to trace sample contamination as it was observed here with NDMA.
Concerning pilot plant samples, only one laboratory was able to quantify the trace level of NDMA, NMOR and the NMEA which were present at concentrations of few tens of ng/kg in solvent. However, NDELA was quantified at higher concentrations by three of the laboratories (see Table 8 ).

Table 8: Quantification of NDELA in pilot plant samples

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

The quantification of NDELA is reliable since, for the 6 pilot plant samples, the results of 3 laboratories present low standard deviations (below 20%). NDELA is one of the most concentrated nitrosamines in degraded MEA solvent.
N-HeGly was also analyzed, but no cross-checking was possible since this was only done by one laboratory. However the results (around 5000 ng/ml in real samples and < 50 in the synthetic) for N-HeGly indicate that this is a major nitrosamine in the real samples.

*4.2. Analysis of total nitrosamines in solvent matrices*

Two of the 5 laboratories propose a method to determine the total of nitrosamine function in solvent samples, the results obtained are presented in Table 9 *(column 2 represents the sum of the weighed nitrosamines in the spiked samples and columns 3 and 4 give the analytical results of each lab).*

Table 9: Results obtained for total nitrosamines analysis of synthetic spiked solutions

| | mg of N-NO/kg of synthetic sample Sum of weighed nitrosamines according to preparation data | LAB A analytical result mg of N-NO/kg of synthetic sample | LAB C analytical result 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 |

The results of the 2 laboratories are very similar, but much higher than the sum of the weighed nitrosamines. Two reasons can be drawn for the gap observed:

- the synthetic solution may contain nitrosamines which have not been intentionally introduced and as a results are not mentioned in the certificate joined, but are quantified by the method of determination of total nitrosamines. However, this is not very likely because, it is expected that the resulting concentrations would have a minor influence compared to those of the weighed nitrosamines.
- the total nitrosamines analytical methods used by the two laboratories greatly overestimate the amount present in the solution.

In any case, further work is necessary on the analysis of total nitrosamines in order to close the gap between analytical results and target values, since the investigated total nitrosamine analysis methods are not capable of reliable quantification of the nitrosamine content in samples in the range of 0.1 – 1.2 mg N-NO/kg sample.

### *4.3. Analyses of specific nitrosamines in flue gas emissions matrices*

The results of analyses presented in Table 10 globally indicate a very good agreement between by the majority of the laboratories for high and low concentration levels. It should be noted that, high relative errors were obtained by the results reported by laboratory D for NDPA, NMOR, and NDELA. For NDPA and NMOR, the measured concentrations were lower than the expected values. This is likely to be due to temperature exposure above 25°C observed from the temperature monitoring during transit as presented in Figure 2. The results of temperature monitoring presented in the following figure indicate that for laboratory D, since the samples were blocked during transport, they have been exposed to temperatures above 25°C for approximately 10 days. As mentioned earlier, nitrosamines are indeed sensitive to temperature; the compounds may degrade due to the elevated temperatures. Concerning the NDELA, the measured concentrations were higher than expected and cannot be attributed to the potential degradation problems as suggested for NMOR and NDPA. Laboratory D utilized a LLE with dichloromethane to concentrate the samples and analysis by LC-MS/MS, in contrast with Laboratory A that used LC-MS/MS without sample pre-treatment. This sample concentration step may have negatively affected the quantitation of specific nitrosamines including NDELA and warrants further methodological investigation prior to successful implementation of this approach for sample extraction and analysis. Accordingly, these results have been excluded from statistical analysis presented in Table 10.

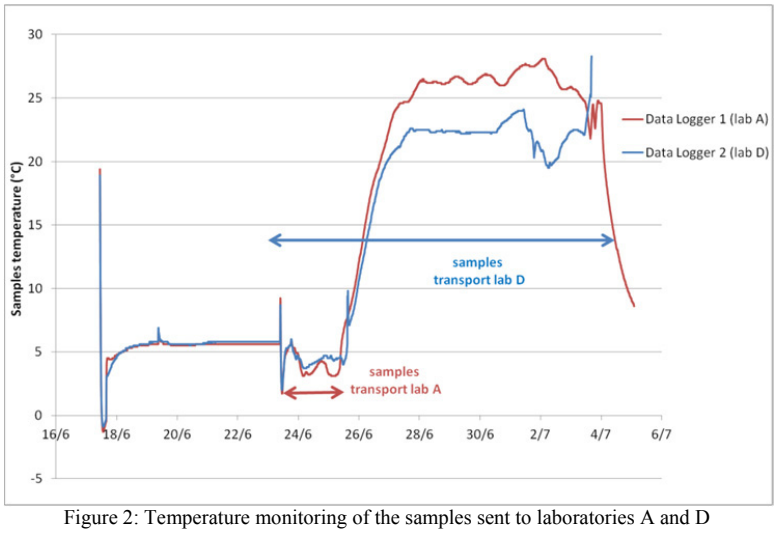



Figure 2: Temperature monitoring of the samples sent to laboratories A and D

For sample A, the relative errors of all results vary between -36% and +25%, with a relative error between mean and theoretical value comprised between -6% and +10%. For sample B, the relative errors are a bit higher since, for all results they vary between -45% and +34%, with a relative error between mean and theoretical value comprised between -13% and +24%; this trend is typical for analytical methods which are generally less precise and accurate at low concentrations compared to high concentrations.

Table 10: Results obtained for sample A (concentrations above 1 ng/ml) and sample B (concentrations below 1 ng/ml)

| | **Results ng/mL sample** | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **SAMPLE A > 1ng/ml** | | | | | | | | | **SAMPLE B < 1 ng/ml** | | | | | | |
| | Target value | Lab A | Lab B | Lab C | Lab D | Lab E | Mean | SD(%) | Target value | Lab A | Lab B | Lab C | Lab D | Lab E | Mean | SD(%) |
| NDMA | 6.3 | 7.2 | 6.2 | 7.7 | NA | 6.2 | 6.8 | 11% | 0.44 | 0.53 | 0.45 | 0.32 | NA | 0.45 | 0.44 | 20% |
| NMEA | 6.3 | 7.0 | 6.1 | 7.8 | NA | 6.0 | 6.7 | 13% | 0.44 | 0.51 | 0.41 | 0.41 | NA | 0.43 | 0.44 | 10% |
| NDEA | 6.4 | 6.7 | 6.4 | 7.6 | NA | 6.5 | 6.8 | 8% | 0.45 | 0.49 | 0.41 | 0.41 | NA | 0.46 | 0.44 | 8% |
| NDPA | 6.5 | 7.1 | 6.1 | 6.2 | 2.4* | 7.1 | 6.6 | 9% | 0.45 | 0.49 | 0.45 | 0.38 | 0.23* | 0.46 | 0.45 | 10% |
| NMOR | 6.5 | 6.8 | 6.0 | 5.6 | 2.0* | 6.4 | 6.2 | 9% | 0.45 | 0.47 | 0.40 | 0.25 | 0.11* | 0.45 | 0.39 | 26% |
| NPYR | 6.5 | 6.6 | 6.1 | 5.3 | 5.6 | 7.5 | 6.2 | 14% | 0.45 | 0.47 | 0.40 | 0.28 | 0.41 | 0.49 | 0.41 | 20% |
| NPIP | 6.5 | 6.8 | 6.9 | 5.0 | 5.4 | 6.6 | 6.1 | 14% | 0.46 | 0.48 | 0.46 | 0.26 | 0.33 | 0.45 | 0.40 | 23% |
| NDBA | 6.5 | 8.1 | 5.9 | 4.2 | 6.5 | 6.9 | 6.3 | 23% | 0.45 | 0.57 | 0.39 | 0.27 | 0.82* | 0.45 | 0.42 | 30% |
| NDELA | 6.5 | 6.8 | NA | NA | 9.8* | 7.5 | 7.2 | 7% | 0.45 | 0.52 | NA | NA | 1.31* | 0.61 | 0.57 | 11% |
| | **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% | | | | |

*results laboratory D probably influenced by degradation processes due to temperature or preparation errors, NA: not analysed

## 5. Conclusions

Within the FP7 OCTAVIUS project, 2 international round robins on the analysis of 9 nitrosamines in solvent matrices and the atmospheric emissions, from the EnBW $CO_2$ capture pilot plant in Heilbronn (Germany) were organized.
The first round robin test was performed on solvent matrices, the analytical methods of the participating laboratories were compared using synthetic spiked samples and real liquid samples obtained from the plant. The main results are the following:

- From round robin on synthetic solutions, mostly reliable results were obtained for the analysis of the main nitrosamines.
- Analyses on real samples from the Heilbronn pilot plant show that most of the laboratories were not able to quantify the nitrosamines since the concentrations were very low. Only one laboratory was able to quantify the trace level of NDMA, NMOR and the NMEA which were present at concentrations of few tens of ng/kg in solvent. The analysis of NPYR, NDEA, NPIP, NDPA and NDBA were under limits of quantification for the 5 laboratories.
- NDELA and N-HeGly were the main nitrosamines detected in real solutions.
- Regarding total nitrosamines analyses, the results obtained by the two laboratories were much higher than the target values. Further work is necessary on the analysis of total nitrosamines since the investigated total nitrosamine analysis methods are not capable of reliable quantification of the nitrosamine content in samples in the range of 0.1 – 1.2 mg N-NO/kg sample.

The second round robin test was performed on atmospheric matrices. Atmospheric emissions from $CO_2$ capture EnBW pilot plant were collected using a sampling train with cold impingers filled in with 0.1M sulfamic acid in water. Each laboratory was provided with two blind samples of the mixture spiked at low (below 1 ng/ml) and high concentration (above 1ng/ml) of nitrosamines. The results obtained showed good agreement for the majority of the laboratories at high and low concentration levels, in spite of the fact that there were significant differences between the laboratories in terms of sample preparation and analytical techniques. From these results, it can be considered that the analysis of specific nitrosamines in sulfamic acid matrices such as those used for $CO_2$ capture using amine based solvents pilot plant atmospheric emissions are well mastered.

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