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Round Robin Tests on Nitrosamines Analysis in the Effluents of a CO₂ Capture Pilot Plant

I. Fraboulet^{a,*}, L. Chahen^b, F. Lestremou^a, A. Grimstvedt^c, B. Schallert^d, B.C. Moeller^e, E. Järvinen^f

^aINERIS, Environment Characterization Dept, Chronical Risk Division, Parc Technologique Alata, BP2, 60550 Verneuil-en-Halatte, France

^bIFP Energies nouvelles, Rond-point de l'échangeur de Solaize, BP 3, 69360 Solaize, France

^cSINTEF Materials and Chemistry, N-7465 Trondheim NORWAY

^dEON Technologies GmbH Alexander-von-Humboldt-Str. 1 D 45896 Gelsenkirchen

^eLovelace Respiratory Research Institute, 2425 Ridgecrest Rd SE, Albuquerque, NM 87108 USA

^fRamboll Analytics, Niemenkatu 73; 15140 LAHTI Finland

Abstract

Processes of post combustion CO₂ 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 CO₂ capture processes matrices is much more challenging since nitrosamines, which are formed to small concentrations as solvent degradation products, may be present in solvent, wash waters, and atmospheric emissions. 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 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 real liquid samples obtained from the plant. The second round robin test was performed on atmospheric emissions collected using a sampling train with cold impingers filled in sulphamic acid in water. Each laboratory was provided with two blind samples of the liquid mixture obtained spiked at different levels of concentrations of nitrosamines

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* Corresponding author. Tel.: +33 344556334; fax: +33 344556302.

E-mail address: isaline.fraboulet@ineris.fr

1. Glossary

LOQ: limit of quantification

SOPs: standard operating procedures

CCS: CO₂ 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

NMEA : N-nitrosomethylethylamine

NDEA : N-nitrosodiethylamine

NDPA : N-nitrosodipropylamine

NMOR : N-nitrosomorpholine

NPYR : N-nitrosopyrrolidine

NPIP : N-nitrosopiperidine

NDBA : N-nitrosodibutylamine

NDELA: N-nitrosodiethanolamine

2. Introduction

Processes of post combustion CO₂ capture using amine based solvents are likely to generate, and emit, not only common pollutants like SO₂, NO_x, CO, CO₂, 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 CCS 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 CCS matrices and the difficulty of measuring nitrogenous compounds in those matrices. Previously, several research groups studied the degradation products of MonoEthanolAmine (MEA), including nitrosamines analysis [2,3], but a comparison of their results has never been tested, measurements were performed on different pilot plants with various analytical methods.

Within OCTAVIUS EU FP7 SP1 subproject, a work package has been dedicated to the promotion of guidelines for the measurement of regulated pollutants (SO₂, NO_x, aldehydes, CO, CO₂, etc) and nitrogenous compounds (amines, nitrosamines, amides, etc) in the three matrices generated by CO₂ capture processes using mine based solvents i.e atmospheric emissions, wash water liquid wastes and circulating solvent. Its aim was to provide recommendations under the form under the form of Standard Operating Procedures (SOPs), to be used as a common methodology.

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

[†] CASTOR CO₂, From Capture to Storage, FP6 project

[‡] CO₂ Enhanced Separation and Recovery, FP7 project

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 of 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 real 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. The target compounds for the round robin are presented in Table 1.

Table 1: Nitrosamines in synthetic samples

Name	Molecular weight (g/mol)	CAS
N-Nitrosodimethylamine (NDMA)	74,08	62-75-9
N-Nitrosomorpholine (NMOR)	116,12	59-89-2
N-Nitrosopyrrolidine (NPYR)	100,12	930-55-2
N-Nitrosomethylethylamine (NMEA)	88,11	10595-95-6
N- Nitrosodiethylamine (NDEA)	102,14	55-18-5
N-Nitrosopiperidine (NPIP)	114,15	100-75-4
N-Nitrosodibutylamine (NDBA)	130,19	924-16-3
N-nitrosodipropylamine (NDPA)	158,24	621-64-7
N-Nitrosodiéthanolamine (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.

In total, the 6 laboratories took part to at least one of the round robin tests. For reason of confidentiality, in the rest of the report, 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.

Table 2 : Methods used during the round robin test on solvent samples

Name	LaboratoryA	LaboratoryB	LaboratoryC	LaboratoryD	LaboratoryE
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	

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

Name	LaboratoryA	LaboratoryB	LaboratoryC	LaboratoryD	LaboratoryE	
NDMA	LC-MS-MS(QQQ) No pretreatment just diluted sample	GC-MS/MS (SPE)	GC-TEA (LLE)	LC-MS/MS LLE of 20 mL of sample with 20 mL DCM – concentrated to 0.5 mL of DCM	GC-HRMS (LLE)	
NMOR			GC-TEA (LLE)			
NPYR			-			-
NMEA			-			
NDEA			-			
NPIP			-			
NDBA			-			
NDPA			-			
NDELA			-			GC-TEA Cation exchange and derivatization

Each laboratory developed its own analytical approach either with or without sample pretreatment or concentration steps. This diversity ensures a better confidence in the results of the round robin tests.

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 laboratories participated. IFPEN provided each participant 5 model samples spiked with nitrosamine (.

Table 1) concentrations ranging from 0.5 ng/mL to 1500 ng/mL and 6 real solvent samples collected during the EnBW campaign in Heilbronn (Germany). This round robin test was focused on specific and total nitrosamine analyses. A detailed description of this round robin and the results are provided in a dedicated report (Octavius Technical Memorandum, IFPEN, June 2014). The synthetic solutions contained 20% CO₂ and had a density of 1.0598 g/cm³. 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. The concentrations of nitrosamines in the 5 synthetic solutions are given in Table 4.

Table 4: Concentrations of nitrosamines in synthetic solutions

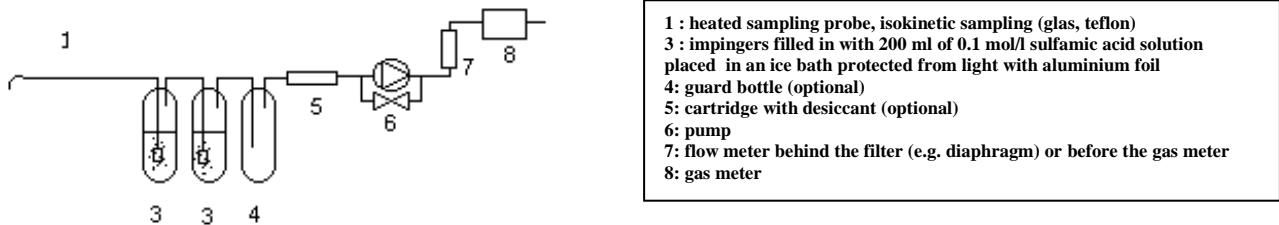
Concentration (µg/kg)	NDMA	NMOR	NPYR	NMEA	NDEA	NPIP	NDPA	NDBA	NDELA
Sample A	14.9	1.3	1.3	1.3	1.3	1.3	155.6	1.3	129.8
Sample B	89.5	75.9	75.9	75.9	75.9	75.9	0.0	75.9	65.0
Sample C	1175.1	162.0	162.0	162.0	162.0	162.0	206.4	162.0	107.5
Sample D	0.8	0.9	0.9	0.9	0.9	0.9	0.8	0.9	43.4
Sample E	39.8	10.8	10.8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

All spiked solutions were prepared by weighting from freshly ordered nitrosamine powders or solutions ordered from 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.

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 the EnBW campaign by collection of flue gas in a solution of sulfamic acid in water using the sampling train described in Figure 1. A detailed description of this round robin and the results obtained is provided in a dedicated report (Octavius Technical Memorandum, INERIS, November 2014).

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 5) resulting in a low (below 1 ng/ml) and a high (above 1ng/ml) level of concentration of nitrosamines.

Table 5: Concentrations of nitrosamines in sulfamic acid in water spiked solutions

	Compound	SAMPLE A > 1 ng/ml	SAMPLE B < 1 ng/ml
N-nitrosodimethylamine	NDMA	6.27	0.44
N-nitrosomethylethylamine	NMEA	6.31	0.44
N-nitrosodiethylamine	NDEA	6.42	0.45
N-nitrosodipropylamine	NDPA	6.47	0.45
N-nitrosomorpholine	NMOR	6.50	0.45
N-nitrosopyrrolidine	NPYR	6.50	0.46
N-nitrosopiperidine	NPIP	6.54	0.46
N-nitrosodibutylamine	NDBA	6.48	0.45
N-Nitrosodiethanolamine	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 6.

Table 6: 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 real 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 7).

Table 7. Quantification of NDELA in real samples

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

The quantification of NDELA is reliable since, for the 6 real 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 8.

Table 8: Results obtained for total nitrosamines analysis of synthetic spiked solutions

	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

The results of the 2 laboratories are very similar, but 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 overestimate the amount present in the solution.

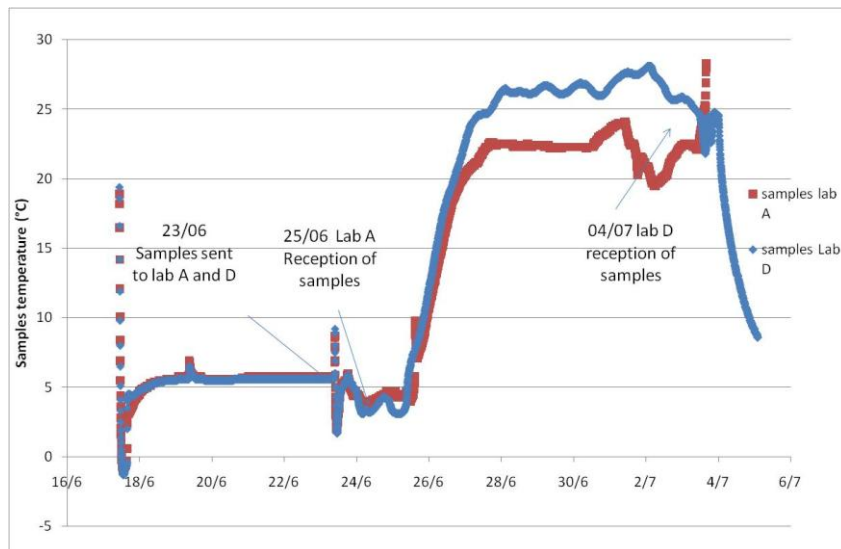
In any case, further work is necessary on the analysis of total nitrosamines in order to close the gap between analytical results and target values.

4.3. Analyses of specific nitrosamines in flue gas emissions matrices

The results of analysis are presented in Table 9. They globally indicate a very good agreement between the results obtained by the different laboratories for high and low concentration levels.

High relative errors have been obtained by laboratory D for NDPA, NMOR, and NDELA, but this is likely to be due temperature exposure above 25°C observed from the temperature monitoring presented in Figure 2. The results of temperature monitoring presented in the following indicate that for laboratory D, since the samples were blocked during transport, they have been exposed to temperatures above 25°C during 10 days. As mentioned earlier, nitrosamines are indeed sensitive to temperature; the compounds may have been through transformations due to this exposure. For data analysis those results have not been taken into account.

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 9: 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 laboratoryD probably influenced by degradation processes due to temperature, results highlighted in yellow obtained without laboratoryD value, NA: not analysed

5. Conclusions

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 higher than the target values. More work is necessary in order to close the gap between analytical results and target values.

The second round robin test was performed on atmospheric matrices. Atmospheric emissions from 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 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 CCS pilot plant atmospheric emissions are well mastered.

6. Acknowledgments:

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7. References

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