Comprehensive monitoring of MEA degradation in a post-combustion CO₂ capture pilot plant with identification of novel degradation products in gaseous effluents.

Ludovic Chahen ^a, Thierry Huard ^a, Lorena Cuccia ^b, Vincent Cuzuel ^b, José Dugay ^b, Valérie Pichon ^b, Jérôme Vial ^b, Camille Gouédard ^a, Leslie Bonnard ^a and Pierre-Louis Carrette ^{a,*}

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

^b Laboratoire Sciences Analytiques Bioanalytiques et Miniaturisation, UMR CBI 8231, ESPCI ParisTech - CNRS, 10 rue Vauquelin, 75005 PARIS, France

Abstract

A pilot plant campaign was performed to study MEA degradation in CO₂ capture conditions and anticipate potential degradation products emissions to the atmosphere in industrial case. Aqueous 30% wt MEA was cycled between absorption and regeneration steps during 1700 hours in the presence of a synthetic flue gas containing 81% of N₂, 14% of CO₂, 5% of O₂, 97 ppm of NO, 9 ppm of SO₂ and 5 ppm of NO₂. Specific methods (sampling, sample conditioning and analysis) were developed to improve degradation products identification and to provide a quantification of targeted compounds in liquid phase and above all in absorber and stripper gas effluents. Especially, trace elements were detected in liquid phase thanks to Head Space-Solid Phase MicroExtraction (HS-SPME) and liquid-liquid extraction with ChemElut cartridges and in gas phase thanks to adsorbent tubes of different type: Sep-Pak[®] for aldehydes and ketones, Orbo 60 for N-nitrosodimethylamine, Tenax and active charcoal for non-specific adsorption. 32 degradation products were identified in liquid phase and 38 in gas phase, 17 of which for the first time, especially derivatives of pyridine and oxazolidine, 1H-pyrrole and a new nitrosamine, the N-nitroso-2-methyl-oxazolidine.

Keywords

Ethanolamine degradation products in gas effluents; pilot plant monitoring; novel analytical methods; solid phase extraction; nitrosamines; stripper gas effluents analysis.

Introduction

Most mature post-combustion CO₂ capture technology is based on CO₂ absorption by aqueous amine solutions. 2-ethanolamine (MEA) remains the benchmark solvent. When a new formulation is developed, it is always compared to MEA in terms of energy requirement of the process, in terms of corrosion and also in terms of degradation of the solvent. Indeed, a main problem associated with chemical absorption using amines is degradation through irreversible side reactions mainly with CO₂ and O₂ but also with NO_x (Fostas et al., 2011) and SO_x (Zhou et al., 2012). These reactions can lead to different consequences for the process: solvent loss causing cost (Carrette et al., 2013; Rao and

Rubin, 2012), formation of volatile compounds potentially unfriendly for environment (Thitakamol et al., 2007), corrosion (Lepaumier et al., 2010, Martin et al., 2012), foaming and fouling (Islam et al., 2011). It is important to list formed compounds and their concentration because some of them could be emitted to atmosphere and could be potentially a concern for human health like nitrosamines for instance (IARC, 1978; NTP, 2012; Thitakamol et al., 2007). Above all, the knowledge of their presence enables the development of adapted counter measures to avoid any risk for environment or human health.

Amine degradation is mainly due to oxidative degradation (Gouédard et al., 2012; Lepaumier et al., 2009b; Rooney et al., 1998; Sexton, 2008) but also to thermal degradation, which occurs at high temperature and high CO₂ partial pressure in the stripper (Davis, 2009; Holub et al., 1998; Lepaumier et al., 2008, 2009a). Oxidative degradation occurs because of a large amount of O₂ in flue gases. These two mechanisms of degradation have been studied mainly under laboratory conditions, sometimes on pilot plant (Reynolds et al., 2015; da Silva et al., 2012; Lepaumier et al., 2011; Strazisar et al., 2003) and rarely on real CO₂ capture process. Most of the studies were focused on solvent analysis. This approach is certainly the most adapted and the simplest method to study the degradation of the solvent. Nevertheless, a lot of degradation products are volatile and it is necessary to consider also gas effluents. Indeed, gas pollutions may have negative impacts on operator but also on the environment (nature or closed population). Environmental acceptance cannot be achieved without a thorough knowledge of all process effluents, gas or liquid, and eventually, adapted cleaning processes. Thus, in this work a complete study of all the effluents of a pilot plant was done during a dedicated campaign. This work exposes a global analytical methodology which can be adapted to the monitoring of any process with any solvent. Especially, a new sampling method based on solid sorbents was developed to identify trace compounds present in gaseous effluents.

Material and Methods

Chemicals

N,N'-(Bishydroxyethyl)oxalamide (**BHEOX**), N-(2-hydroxyethyl)acetamide (**HEA**) (90 %), N-(2-hydroxyethyl)formamide (**HEF**) (97 %), 2-methyloxazoline (≥ 99 %) and 3-methylpyridine (99 %) were purchased from Alfa Aesar (Schiltigheim, France). Glycolic acid, potassium acetate, sodium formate, sodium propionate, sodium nitrite, magnesium sulphate, oxalic acid, lithium nitrate, potassium hydroxide, formic acid, formaldehyde (37%), dimethylamine solution (40 wt%), acetamide (99%), acetic acid (>99.7%), ethyleneglycol (**EG**) (99.8%), 1H pyrrole (98%), N,N-dimethylformamide (**DMF**) (99.8%), pyrazine (>99%), 2-oxazolidinone (**OZD**) (98%), 2-methylpyrazine (**2MP**) (>99%), diethyleneglycol (**DEG**) (>99%), triethyleneglycol (**TEG**) (>99%), 2-ethylpyrazine (>98%), 2,3-dimethylpyrazine (>95%), N-hydroxyethylimidazole (**HEI**) (97%), bicine, N-(2-hydroxyethyl)ethylenediamine (**HEEDA**), N,N-bis-2-(hydroxyethyl)ethylenediamine (**BHEEDA**) (97%), N-(2-hydroxyethyl)imidazolidin-2-one (**HEIA**), diethanolamine (**DEA**) (>98%), 2,5-dimethylpyrazine (>98%), ethanolamine (**MEA**) (98 %), N-nitrosodimethylamine (**NDMA**), N-nitrosodiethanolamine (**NDELA**), N-Nitroso-N,N-diethylamine (**NDEA**) and N-nitrosomorpholine (**NMOR**) were purchased from Sigma-Aldrich (Saint Quentin Fallavier, France). Oxazoline (96 %) was purchased from Interchim (France). 4-(2-hydroxyethyl)piperazin-2-one (**4HEPO**) and N-(2-hydroxyethyl)pyrrole (**HEPyr**) (99 %) were purchased from Tygersci (Hopkinsville, USA). N-(2-hydroxyethyl)glycine (**HEGly**) (95 %) was

purchased from Enamine (Kiev, Ukraine). Glycine (99.7 %) was purchased from Merck (Lyon, France). Oxazolidine was purchased from Selectlab (Münster, Germany). 2,6-dimethylpyrazine, 2-ethyl-6-methylpyrazine, 2-ethyl-5-methylpyrazine and 2-ethyl-3-methylpyrazine were purchased from SAFC (Sigma-Aldrich, Saint Quentin Fallavier, France). N,N'-Bis-(2-hydroxyethyl)urea (**BHEU**) was purchased from Chemos GMBH (Regenstauf, Germany). 1-(2-Hydroxyethyl)piperazinone hydrochloride (**1HEPO**) was purchased from Ukrorgsyntez (Kiev, Ukraine). Methanol, acetonitrile and ethylacetate were purchased from Carlo-Erba (Val de Reuil, France).

Ultra-pure water was produced using a Direct-Q UV 3 system (18.2 MΩ.cm) from Millipore (Molsheim, France).

N-nitroso-2-methyl-oxazolidine was synthesized according to the protocol of Saavedra (Saavedra, 1981). N,N'-bis(2-hydroxyethyl)piperazin-2,5-dione (**2,5-BHEPDO**) and 2-methyloxazolidine were synthesized according to Gouedard *et Al.* (Gouedard, 2014).

Pilot plant description

IFPEN pilot plant uses two columns of around 1 meter each with a diameter of 5 cm. The first one is used as an absorber (C10) where the solvent (30 % wt of MEA in water) is loaded in CO₂ (Figure 1). The second column is used as a stripper (C20) where the solvent is regenerated and CO₂ is released. Each column is equipped with high performance packings for ensuring good gas/liquid mass transfer: The absorber contains DX packing and the stripper contains BX packing.

Figure 1. Scheme of IFPEN pilot plant

The campaign lasted around 1700 hours. Synthetic flue gas contained 80.7% of N₂, 14.1% of CO₂, 5.1 % of O₂, 97 ppm of NO, 9 ppm of SO₂ and 5 ppm of NO₂. Total absolute pressure of the absorber was 1,2 bar. The gas flow rate was 1000 NL/h at 40°C and the solvent flow rate was 2 L/h. The total

volume of solvent was 20 liters. Absorber outlet gas was directed to a heat exchanger (E10) to condensate water. Condensates was separated from gas phase in separator V10. Heat exchanger E10 followed by separator V10 may be considered as a low efficiency water wash section: E10 cooling liquid temperature is 4°C and E10 outlet gas temperature is 15°C enabling large amount of water condensation and therefore partial MEA and degradation products dissolution. V10 condensates was mixed with CO₂ lean amine in tank T-01. Once loaded with CO₂, CO₂ rich amine was pumped with P02 and heated at 100°C in charge/effluent exchanger E21 before entering at the top of the stripper. The stripper was heated at 125°C which enabled the regeneration of the amine and the release of CO₂. Released CO₂ was directed to a heat exchanger (E20) to condensate water. The condensate was separated in separator V20 and was reintroduced at the top of the stripper with the CO₂ rich amine. At the bottom of the stripper, the CO₂ lean amine was cooled in charge/effluent exchanger E21 then in exchanger E40 to be introduced in tank T-01 at a temperature close to room temperature. CO₂ lean amine is pumped from T-01 with P01 and heated at 40°C to be introduced at the top of absorber. MEA concentration was maintained between 30 and 35 % wt during the campaign by water addition in tank T-01. At the end of the campaign, concentrations of Iron, Nickel and Chromium, measured by Inductively Coupled Plasma with Optical Emission Spectroscopy (ICP-OES) were less than 5 mg/kg. Thus, corrosion was assumed negligible.

Analysis

Ionic chromatography

Ion chromatography was commonly used to quantify acids in their anionic form: glycolate, formate, acetate, oxalate, sulfate, nitrite, and nitrate ions. The concentration of CO₂-species (carbamate, carbonate and bicarbonate ions and carbonic acid) was also determined by Ionic Chromatography to determine CO₂ loading of amine given as mol CO₂/mol MEA. Samples were diluted in ultrapure water. 25 µL of solution were injected twice on a Dionex ICS-3000 ion chromatograph (ThermoFisher Scientific, Villebon-sur-Yvette, France). The column was an AS-15 (4 × 250 mm). Eluent was aqueous KOH solution with a concentration gradient (from 8 to 60 mM) at a flow rate of 1 mL.min⁻¹. Detector was a conductimeter. A run of 60 minutes enabled an optimal separation. Some samples were pre-treated with HNO₃ 69 % to reach a pH below 4 to eliminate MEA carbamate peak which overlaps acetate and glycolate peaks. Quantification of anions was obtained with an uncertainty of ± 10%. Quantification of CO₂ loading was obtained with an uncertainty of ± 15%.

LC-MS/MS

Analyses were performed on a LC Thermo Scientific Dionex Ultimate 3000 (Analytical Autosampler WPS-3000SL, Quaternary Analytical Pump LPG-3400SD) coupled with a MS Thermo Scientific TSQ Quantum Access MAX with HESI-II source (ThermoFisher Scientific, Villebon-sur-Yvette, France). It was used in positive mode, probe in position C, electrospray voltage of 2500V and capillary temperature of 200°C. The sheath gas was nitrogen at a flow rate of 40mL/min and the auxiliary gas at 8 mL/min. Chromatographic separations were conducted on a Thermo HyperCarb column (PGC) 150 mm x 3 mm, 5 µm-particles (ThermoFisher Scientific, Villebon-sur-Yvette, France). The mobile phase was a mixture of (A) water with 0.1% formic acid and (B) methanol with 0.1% formic acid at a flow rate of 350µL/min. 5 µL of sample were injected. A pre-run rinse of 100% A for 8 min was performed, then the solvent gradient started at 100% of A for 10 min before reaching a ratio of 80:20 (A:B v:v) in 8 min. This ratio was maintained for 12 min. Samples had to be at least 1000-fold diluted before injection to prevent the mass spectrometer from being polluted by MEA. The MRM

transitions of the targeted compounds used are given in supplementary material. They are reported from the literature or determined with standards. Quantification was obtained with an uncertainty of $\pm 20\%$. Two internal standards were used: Diethanolamine-d8 for DEA, HEGly and BHEU, and Glycine-d5 for Glygly and Gly. Compounds quantification method and performances are detailed in our previous work (Cuzuel et al., 2014).

GC-FID

MEA concentration was determined by GC-FID performed on Agilent HP6890 chromatograph (Agilent Technologies, Massy, France) with a carbowax amines column (15 m x 0.53 mm, 1 μm) made by Supelco (Sigma-Aldrich, Saint Quentin Fallavier, France) and with triethyleneglycol as internal standard. The oven program started at 100 °C then the temperature was raised at 8°C/min to 200 °C and held for 5 min. 1 μL of the sample was injected in the inlet at 250°C and the split flow was 100 mL/min. The Helium gas flow was 8mL/min with a top column pressure of 4.2 psi. Quantification was obtained with an uncertainty of $\pm 5\%$.

GC-MS

Analyses were performed on an Agilent 7890A gas chromatograph coupled with an Agilent 5975C inert XL MSD mass spectrometer (Agilent Technologies, Massy, France). The device was equipped with a MPS (MultiPurpose Sampler) auto sampler from Gerstel (RIC, Saint-Priest, France) that enabled fully automated HS-SPME analyses. Two columns (Chromoptic, Villejust, France) were used to separate all the target compounds, a non-polar fused silica capillary column CP-SIL8 CB-MS (30 m x 0.25 mm, 1 μm) and a polar fused silica capillary column DB-WAX (30 m x 0.25 mm, 0.5 μm). For the non-polar column, initial temperature was 40°C held for 2 min then raised to 130°C at 7°C/min, increased to 280°C at 13°C/min and held for 10 min. For the polar column, oven temperature program started at 40°C, held for 2 min then raised to 130°C at 7°C/min, then increased to 200°C at 10°C/min and held for 7 min. In both cases, helium was used as carrier gas in constant flow mode at 1 mL/min. The transfer line temperature to the MS detector was set at 280°C. For liquid injection procedures, real samples were diluted 10 times in methanol before injecting 1 μL in split mode (1:5) at 250°C. Quantification of a selection of products was obtained with an uncertainty of $\pm 15\%$.

For thermodesorption of tubes, gas flow rate of helium was 40 mL/min in splitless mode. Initial temperature of desorption was 35°C held for 2 min then raised to 300°C at 120°C/min and held for 6 min. Desorbed molecules were cryofocused in the injector at -40°C with liquid CO₂. Then temperature increased from - 40°C to 300°C at 12°C/s and the molecules were injected in the column in splitless mode. The same GC/MS method as for liquid samples was used.

Detection was performed with a mass spectrometer using electronic ionization (EI) or chemical ionization (CI) source. The latter was both used in positive (PCI) and negative (NCI) mode. The EI source (70 eV) was heated to 250°C, the scan range was 25 to 250 amu. As for the CI source, it was heated to 300°C for positive mode and to 150°C for negative mode, CH₄ was used as reactant gas and the scan range was 50 to 250 amu.

Some complementary analyses were also performed on a Thermo Finnigan Tempus (GC-TOF (Time of flight)/MS) (Thermo Finnigan, Villebon-sur-Yvette, France), which was used with CP-SIL8 CB-MS (30 m x 0.25 mm, 1 μm) (Chromoptic, Villejust, France). Initial temperature was 35°C then raised to 230°C at 3°C/min and held for 50 min. Helium was used as carrier gas in constant flow mode at 0.9 mL/min. The transfer line temperature to the MS detector was set at 250°C. Mass spectrometer was used with the EI source (70 eV) heated at 200°C. The scan range was 10 to 350 amu.

GC-HRMS

Analyses were performed on an Agilent 7890A gas chromatograph (Agilent Technologies, Massy, France) coupled with Autospec Premier mass spectrometer from Waters (Saint-Quentin-en-Yvelines, France). A capillary column DB5-MS (30m x 0.25 mm, 0.50 μ m) (Chromoptic, Villejust, France) was used to separate target compounds. Initial temperature was 35°C held for 4 min then raised to 150°C at 10°C/min, increased to 250°C at 20°C/min. Helium was used as carrier gas in constant flow mode at 1.5 mL/min. Inlet temperature was 230°C, the split ratio was 1: 5 and the volume injected was 0.8 μ L. The transfer line temperature to the MS detector was set at 260°C. Detection was performed with a magnetic sector mass spectrometer using electronic ionization (EI) source in positive mode. The EI source (35 eV with trap 450 μ A) was heated to 250°C. The mass spectrometer was used in a Single Ion Recording mode (SIR) with a scan rate of 0.5 s, an interscan of 0.2 s and a resolution comprised between 5000 and 6000. The recording ion mass were m/z = 74.0480 Th for NDMA and m/z = 116.0590 Th for NMOR.

Head Space –SPME

For Head Space – SPME (HS-SPME) procedures, the volume of sample introduced in the 20 mL HS vial was 5 mL. The fully automated HS-SPME procedure was as follows. First, the vial was equilibrated at 70°C during 5 min then the 75 μ m Carboxen/PDMS fibre SPME, obtained from Supelco (Sigma-Aldrich, Saint Quentin Fallavier, France) was placed into the head-space of the sample for the extraction, still maintained at 70°C for 30 min. At the end of the extraction, the fibre was desorbed directly in the injector set of the GC/MS at 250°C in split mode (1:5). This method was initially developed for identification and quantification of pyrazines (Rey et al., 2013). It is adapted here to the identification of other degradation products present in liquid phase.

FT-IR

A FT-IR disposal provided by GASMET (SISTEC, Vienne, France) was used to monitor different gas effluents (see the computer symbols on Figure 1). It enabled the monitoring of several products in gas phase, especially ammonia, CO₂, NO, NO₂ and SO₂. Limit of Detection (LOD) and uncertainties were determined by the equipment provider. The uncertainty is 2 % of the full scale. Used range and LOD are given in Table 1.

Table 1: Range and LOD values of FTIR analysis

Gas	Range (molar)	LOD
NH ₃	0-4000 ppm	0,3 ppm
CO ₂	0-100 %	200 ppm
SO ₂	0-10000 ppm	1 ppm
NO	0-2500 ppm	4 ppm
NO ₂	0-200 ppm	1 ppm

Gas sampling

Gas sampling was performed to analyze degradation products which were not observed by FT-IR. Solid phase extraction (SPE) of gaseous compounds was performed during 1 or 19 hours in function of solid adsorbent type. During gas sampling, the gas flow in the absorber was reduced to 500 NL/h and the solvent flow was reduced to 1 L/h. Gas samplings have been done after the separator V10 every two weeks and once after the separator V20 at the end of the campaign.

Assisted Liquid-Liquid Extraction (ALLE)

An original sample handling approach using assisted liquid-liquid extraction on diatomaceous earth cartridges (ChemElut) (Agilent Technologies, Massy, France) allowed to extract selectively nitrosamines from samples. This extraction on solid matrix allowed to eliminate a large amount of MEA and thus enhanced the extraction of nitrosamines (improvement in sensitivity of an order 5 to 10). 2 mL of phosphate buffer (pH = 7.4) were mixed with 1 mL of sample. This mixture was adsorbed during 5 min on ChemElut (3mL). Then, elution was performed with 9 mL of ethyl acetate. Solution was smoothly evaporated with the help of a nitrogen flux gas to 0.25 mL and redissolved in 100 µL of ultrapure water. Sample were then directly analyzed with LC-MS/MS.

Solid phase extractions (SPE)

A device enabling simultaneous adsorption on four different solid phase extraction tubes was implemented on outlet gas lines after V10 and V20. After V10 and V20, gas temperature (15°C) was below room temperature avoiding any water condensation in tubes. Gas flow rate was regulated with a flow meter in order to respect the maximum flow rate specified by tubes suppliers. For each adsorbent type, three tubes were used in series to enable quantification of the retained products in case of saturation or piercing of the two first tubes. The sampling conditions are given in Table 2.

Table 2: Sampling conditions and SPE tubes according to target compounds

Target Compounds	Tubes References	Gas flow (NL/h)	Sampling time (h)
Aldehydes and ketones	Sep-Pak [®] DNPH	6	1
Nitrosamines	ORBO 60	10	19
Volatile compounds	Tenax TA TDU	6	1
Volatile compounds	Activated charcoal	6	1

Sep-Pak[®] tubes (Sigma-Aldrich, Saint Quentin Fallavier, France) containing 2,4-Dinitrophénylhydrazine (DNPH) were analyzed by the French institute INERIS (Verneuil-en-Halatte, France). Sep-Pak[®] tubes were chemically desorbed with 2 mL of acetonitrile and products were analyzed by High Performance Liquid Chromatography (HPLC) with diode array detector (DAD). Aldehydes were quantified by external calibration according to the method INRS Métropol 001. Excepted for formaldehyde, all aldehydes were absorbed at more than 99% in the first tube. Quantification was obtained with an uncertainty of ±30%.

Thermosorb/N are the best sorbents to analyze nitrosamines because they are free of artifacts formation (Roundbehrer et al., 1980). However, these sorbents were not available for our study. Therefore ORBO 60 tubes were used. They contain a Florisil phase (Sigma-Aldrich, Saint Quentin Fallavier, France) which is particularly efficient to adsorb nitrosamines and especially NDMA which is one of the most volatile and one of the most carcinogenic nitrosamine potentially present in CCS gas effluents. Florisil sorbent are known to form slightly NDMA artifacts (Roundbehrer et al., 1980). In this study, only NDMA was quantified. Orbo 60 tubes were chemically desorbed twice with 2 mL of ethylacetate. Results showed that 2mL were sufficient to elute more than 95% of NDMA. NDMA was quantified by GC/HRMS. NDMA was adsorbed at more than 90% in the first tube.

Tenax TA TDU tubes (Gerstel, Saint-Priest, France) were thermally desorbed. Tenax is a porous polymer widely used as an adsorbent in both air collection and purge and trap applications. Its

structure provides alternate adsorption/desorption of a wide variety of compounds. Quantification of a selection of products was obtained with an uncertainty of $\pm 30\%$. Activated charcoal tubes (Gerstel, Saint-Priest, France) were used as non-specific adsorbent such as Tenax TA TDU tubes. The large surface area of this carbon form enables excellent adsorption/desorption of a wide variety of volatile compounds. The activated charcoal tubes were also thermally desorbed. Tenax TA TDU tubes enabled to adsorb larger amounts of products but activated charcoal tubes were useful to confirm (or infirm) punctually the presence of some volatile compounds observed with Tenax tubes. Indeed, some products detected on Tenax might be due only to the degradation of the Tenax phase in gas effluent conditions and it was necessary to be able to cross the results between the two different adsorbent phases.

Results and Discussion

Pilot plant monitoring

Gas online FTIR analyses enabled to study the composition of the gas, in terms of major compounds, at the different point of the pilot plant Table 3 gives CO_2 , SO_2 , NO and NO_2 concentrations at the inlet and outlet of absorber and stripper. NH_3 concentration was between 10 and 20 ppm vol at C10 exit during the whole campaign.

Table 3: Gas composition in C10 and C20 outlet gases after condensation step (LOD: Limit Of Detection).

Gas	Inlet C10	Exit C10 dry gas	Exit C20 dry gas
CO_2	14,1 %	6,5 %	99,99 %
SO_2	9 ppm	2 ppm	< LOD
NO_2	5 ppm	< LOD	< LOD
NO	97 ppm	83 ppm	50 ppm
O_2	5,1 %	5,1 %	Not analyzed
N_2	80,7%	88 % (calculated)	-

Based on the total inlet flow rate and assuming that nitrogen did not absorb and that O_2 consumption was negligible, CO_2 capture yield was around 60 % which corresponds to 282 kg of CO_2 treated in around 1700 hours. Solvent sampling was done three times a week at the bottom of the absorber (C10) for the CO_2 rich amine and in the tank T-01 for the CO_2 lean amine. All samples were stored in brown flaks between 4 and 8°C. The campaign monitoring consisted in analyzing the concentrations of MEA, CO_2 -species and anions. The concentration of MEA was determined by GC-FID enabling also an estimation of water loss (Figure 2). The pilot lost approximately 1,5 L of water per week in V10 and V20 outlet gases. Water loss was compensated by water addition (Figure 2). 14,4 kg of water were added during the campaign. Some MEA was lost also because of sampling. Initially 20 kg of 30% wt MEA in water was introduced in the pilot plant. 1,3 kg of 30 % wt MEA solution were therefore added during the campaign. MEA concentration was then maintained between 30% and 35% wt during the whole campaign. The concentration of CO_2 -species (carbamate, carbonate and bicarbonate ions and carbonic acid) was determined by Ionic Chromatography to determine CO_2 loading of amine given as mol CO_2 / mol MEA. CO_2 loading was close to 0,3 for CO_2 lean amine and 0,5 for CO_2 rich amine in stationary conditions (Figure 3). The concentration of

formate, acetate, oxalate, glycolate, propionate, nitrite, nitrate and sulfate (heat stable salts) was determined by ionic chromatography.

Figure 2. Evolution of MEA concentration in T01 (CO₂ lean amine) and added water quantities

Figure 3 shows that CO₂ loading in the solvent at the exit of absorber and stripper was quite stable at roughly 0,5 and 0,3 mol/mol respectively.

Figure 3. Evolution of CO₂ loading in CO₂ lean amine and in CO₂ rich amine

Two kinds of heat stable salts (HSS) were formed: the ones due to flue gas impurities such as NO₂ or SO₂ and the organic ones due to solvent oxidative degradation. Figure 4 shows the evolution of nitrates, nitrites and sulfates during the campaign.

Figure 4. Evolution of nitrates, nitrites and sulfates

The evolution of sulfates was almost linear from the beginning to the end of the campaign as expected. The concentration of sulfates reached 2416 mg/kg in 1701 hours. It means that 94 % of the total amount of injected SO₂ gave sulfates if SO₂ concentration at absorber exit is taken equal to 2 ppm mol which is the detection limit of FTIR. Nitrites concentration was quite constant at around 19 ppm from 69 to 1701 hours which may indicate that nitrites are some kind of intermediates. They were formed and consumed throughout the campaign, mainly due to their oxidation into nitrates which reached 383 mg/kg at 1701 hours. Nitrates and nitrites are mainly due to the presence of NO₂ and NO in flue gas but they may also be a resultant of MEA degradation. Table 4 gives the mass balance between NO₂/NO absorbed in solvent based on FTIR results and nitrates/nitrites accumulation in the solvent at the middle and at the end of the campaign.

Table 4: Comparison of concentration of products formed from introduced NO_x with nitrates and nitrites concentration

Time (h)	Calculated concentration of products formed from introduced NO _x (mol/kg)	Total concentration of analyzed nitrates and nitrites (mol/kg)	Ratio
836	4,12E-02	4,23 ± 0,4 E-02	1,0
1701	8,39E-02	1,45 ± 0,15 E-01	1,7

In the middle of the campaign measured nitrites/nitrates are close to NO₂/NO absorption. But at the end of the campaign, the amount of nitrites/nitrates exceeds NO₂/NO absorption because the proportion due to MEA degradation increased. On the other hand, they may be also consumed to form other degradation products like nitrosamines but this contribution is less important.

A quantitative monitoring of organic HSS was focused on formates, glycolates and oxalates (Figure 5).

Figure 5. Evolution of formates, glycolates and oxalates

Evolution of formates was almost linear and the concentration reached 195 mg/kg at 1701 hours. It is the main organic acid formed by MEA degradation as expected (Vevelstad et al., 2013). Glycolates were already present in supplied MEA and their concentration fluctuated between 60 and 100 mg/kg during the campaign without significant evolution. Organic acids are known to be starting material of many degradation products (Gouedard et al., 2012) which may explain such a constant concentration. On the other hand, oxalates concentration was lower than the limit of quantification of the analytical method until 812 hours and reached 39 mg/kg at 1701 hours. Expected acetates and propionates (Cuzuel et al., 2015) have not been detected at all during this campaign. Acetates are assumed to have mainly reacted with MEA to form N-(2-hydroxyethylacetamid (HEA) (see table 4). On the other hand propionic acid was not present neither as propionate nor as N-(2-hydroxyethylpropanamide). In our previous work (Cuzuel et al., 2015) both were observed but MEA was more concentrated than in the present work: 40% wt instead of 30% wt. Therefore, in present work, degradation is slower and they might be detectable after a longer running time.

Degradation products in the solvent

Organic products identified in the solvent throughout the campaign are given in Table 5. The main degradation products described in our previous paper (Cuzuel et al., 2015) were observed here. Nevertheless, our previous pilot plant campaign was done with 40% wt MEA enabling higher concentrations of degradation products. That is why less degradation products were observed in this work but all should be observed after a longer running time. Each degradation product identification was confirmed by corresponding standard analysis and a mechanism of formation was proposed for each one (Gouedard et al., 2014a; Gouedard, 2014b; Rey et al., 2013). For each identified molecule, the corresponding standard was purchased or synthesized. Identification was confirmed by obtaining the same mass or NMR spectrum.

Table 5: Degradation products detected in the solvent

			Analysis methods				
			GC-MS TOF	GC-MS		LC-MS-MS	GC-HRMS
Specific sample treatment →			Ø	Ø	HS-SPME	Ø	Extraction
Products	Mw g/mol	CAS					
Ethyleneglycol (EG)	62	107-21-1		X			
1H-Pyrrole	67	109-97-7			X		
Oxazoline	71	504-77-8			X		
Oxazolidine	73	504-76-7		X	X	X	
N-nitrosodimethylamine (NDMA)	74	62-75-9					X
Glycine	75	56-40-6				X	
Pyrazine	80	290-37-9	X		X (*)		
2-Methyloxazoline	85	1120-64-5	X				
2-Oxazolidinone (OZD)	87	497-25-6	X	X	X (*)		
N-(2-hydroxyethyl)formamide (HEF)	89	693-06-1	X	X			
2-Methylpyrazine (2MP)	94	109-08-0			X (*)		
N-(2-hydroxyethyl) acetamide (HEA)	103	142-26-7		X			
N-(2-hydroxyethyl) ethylenediamine (HEEDA)	104	111-41-1		X		X	
Diethanolamine (DEA)	105	111-42-2				X	
2,5-dimethylpyrazine	108	123-32-0			X		
2-ethylpyrazine	108	13925-00-3			X		
N-(2-hydroxyethyl)pyrrole (HEPyr)	111	6719-02-4			X		
N-(2-hydroxyethyl)imidazole (HEI)	112	3699-54-5		X			
N-nitrosomorpholine	116	59-89-2					X
N-(2-hydroxyethyl)glycine (HEGly)	119	5835-28-9				X	
2-ethyl-6-methylpyrazine	122	36731-41-6			X		
2-ethyl-5-methylpyrazine	122	236-416-6			X		
2-ethyl-3-methylpyrazine	122	15707-23-0			X		
N-(2-hydroxyethyl)imidazolidin-2-one (HEIA)	130	3699-54-5				X	
N-nitrosodiethanolamine (NDELA)	134	1116-54-7				X	
1-(2-hydroxyethyl) piperazin-2-one (1HEPO)	144	59702-23-7		X			
4-(2-hydroxyethyl) piperazin-2-one (4HEPO)	144	23936-04-1	X	X			
N,N'-bis(2-hydroxyethyl) ethylenediamine (BHEEDA)	148	3197-06-6				X	
N,N'-Bis-(2-hydroxyethyl)urea (BHEU)	148	15438-70-7				X	
Bicine	163	150-25-4				X	
N,N'-(Bishydroxyethyl)oxalamide (BHEOX)	176	1871-89-2		X			
N,N'-bis(2-hydroxyethyl)piperazin-2,5-dione (2,5-BHEPDO)	202	23936-14-3		X			

361 (*) present in initial solution at lower concentration

362 Some of these products were present at a high enough concentration to monitor them quantitatively
 363 during the campaign. Diethanolamine (DEA), N-(2-hydroxyethyl)glycine (HEGly) and N,N'-Bis-(2-
 364 hydroxyethyl)urea (BHEU) were quantified by LC-MS-MS (Figure 6). Ethyleneglycol (EG), N-(2-

hydroxyethyl)formamide (HEF), N-(2-hydroxyethyl)acetamide (HEA) and oxazolidinone (OZD) were quantified by GC/MS (Figure 7). Their proportions were globally in agreement with state of art (da Silva et al., 2012; Vevelstadt et al., 2013). Nevertheless, there were some differences. HEgly was not the main degradation product in our case. The first reason is that this compound is an intermediate to some other degradation products (Gouedard, 2014b) whose formation may be conditions dependent. The second reason is that the main product in our case was BHEU which was never quantified by other authors to the best of our knowledge. Its formation may be explained by a reaction between MEA carbamate and MEA: nucleophilic attack of MEA amine function on carbamate carbonyl group as in the case of imidazolidinones formation which are cyclic ureas (Lepaumier et al., 2009a). The high concentration of both reagents may explain the high concentration of BHEU.

Figure 6. LC-MS-MS monitoring of DEA, HEGly and BHEU during the campaign.

Figure 7. GC-MS monitoring of EG, HEF, HEA, 1HEPO, 4HEPO and OZD during the campaign

OZD concentration increased rapidly during the first 500 hours before reaching a kind of maximum at 0.9 g/L. OZD is an intermediate easily formed by carbamate cyclisation but it is also easily consumed by reaction with nucleophilic compounds (Lepaumier et al., 2009c): it reacts especially with amine functions of MEA and its degradation products. HEF was already present in supplied MEA at 0.2g/l and kept quite constant during the campaign: it is formed from MEA and formic acid (Gouedard et al., 2012) and is also an intermediate to other degradation products as oxazoline for example (Gouedard et al., 2014a). On the contrary, 4HEPO started relatively slowly but seemed to increase more rapidly after 1000 hours. Several mechanisms are proposed for 4HEPO formation (Gouedard, 2014b). In any case, starting material is a degradation product of MEA: HEEDA or HEGly. Therefore their accumulation during the campaign may explain 4HEPO evolution. In this work 4HEPO concentration was much higher than HEGly contrary to Da Silva et al. results (Da Silva et al., 2012) suggesting that our conditions promoted HEGly consumption to form 4HEPO. 1HEPO was less concentrated than 4HEPO because its formation is less favorable (Gouedard, 2014b).

Nitrosamines are the subject of a growing interest in the CCS literature due to their potential carcinogenic properties. Three nitrosamines were identified in liquid phase in this work: N-nitrosodiethanolamine (NDELA), N-nitrosomorpholine (NMOR) and N-nitrosodimethylamine (NDMA). N-nitroso-HEGly observed by Morken et al. couldn't be confirmed here because the corresponding standard couldn't be provided (Morken et al., 2014). Some other nitrosamines were only identified in the gas phase as shown below. NDELA could not be quantified accurately by our method but its concentration was definitely superior to our limit of detection 50 µg/kg. The NMOR was detected but its concentration was inferior to our limit of quantification of 4 µg/kg. Finally, the concentration of NDMA was determined in both CO₂ rich and CO₂ lean amine (Table 6).

402

Table 6: Concentration of NDMA in CO₂ lean and CO₂ rich amine determined by GC-HRMS

Concentration of NDMA in µg/kg	400 hours	1400 hours
lean amine (T01)	317 ± 63	541 ± 108
rich amine(C10)	265 ± 53	446 ± 89

403

404 Concentrations of NDMA in CO₂ rich and CO₂ lean amine are equivalent if higher loading of CO₂ in
 405 rich amine compared to lean amine (dilution of nitrosamine) and uncertainty of the method are
 406 taken into account. These concentrations are quite high comparing to other results in the literature
 407 (Einbu, 2013) and that could be due to the IFPEN pilot specifically. However, NDMA is known to be
 408 carcinogenic and volatile. Thus, the monitoring of the degradation products in the gas effluent in CCS
 409 plant is definitely needed.

410 Degradation products in gas effluents

411 The analysis of degradation products in gas effluent was based on different sampling methods using
 412 solid phase extraction. Tenax and activated charcoal adsorbents were used as non-selective
 413 adsorbents. Orbo 60 adsorbents were dedicated to the analysis of nitrosamines. Sep-Pak[®] tubes
 414 containing 2,4-Dinitrophénylhydrazine (DNPH) were used to adsorb aldehydes and ketones. These
 415 analytical campaigns were achieved on gas effluents after the condenser V10 of the absorber and
 416 after the condenser V20 of the stripper. Table 7 shows degradation products identified with Tenax,
 417 activated charcoal and Sep-Pak[®] tubes. Compounds written in bold are novel compounds which have
 418 never been detected in CCS literature so far to the best of our knowledge. Some of them were also
 419 identified in our previous work dedicated to liquid phase analysis (Cuzuel et al., 2015).

Table 7: Degradation products detected on Tenax, activated charcoal and Sep-Pak® tubes in gas effluents

Products	CAS	Mw (g/mol)	Absorber			Stripper	
			Tenax	Activated charcoal	Sep- Pak®	Tenax	Sep- Pak®
Formaldehyde	50-00-0	30			X		X
Acetaldehyde	75-07-7	44	X		X		X
Dimethylamine	124-40-3	45	X	X			
Propionaldehyde	123-38-6	58			X		X
Acetamide	60-35-5	59				X	
Acetic acid	64-19-7	60	X				
Ethyleneglycol (EG)	107-21-1	62	X	X		X	
1H-pyrrole	109-97-7	67	X	X		X	
2-butenal	4170-30-3	70	X			X	
Oxazoline	504-77-8	71	X	X			
Butyraldehyde	123-72-8	72					X
2-butanone	78-93-3	72	X	X		X	X
N,N-dimethylformamide (DMF)	68-12-2	73	X	X			
Oxazolidine	504-76-7	73	X	X		X	
Propionic acid	79-09-4	74	X				
N-nitrosodimethylamine (NDMA)	62-75-9	74	X	X			
Pyrazine	290-37-9	80	X	X		X	
2-methyloxazolidine	16250-70-7	87	X			X	
2-oxazolidinone (OZD)	497-26-6	87	X			X	
2-methylpyridine	109-06-8	93	X			X	
3-methylpyridine	108-99-6	93	X			X	
2-methylpyrazine (2MP)	109-08-0	94	X	X		X	
2-ethyloxazolidine	16250-71-8	101	X			X	
N-Nitrosodiethylamine	62-75-9	102	X	X			
Diethyleneglycol (DEG)	111-46-6	106	X				
2-ethylpyridine	100-71-0	107				X	
2,3-dimethylpyridine	583-61-9	107				X	
3-ethylpyridine	536-78-7	107				X	
2,6-dimethylpyrazine	108-50-9	108	X	X			
2-ethylpyrazine	13925-00-3	108	X				
2,3-dimethylpyrazine	5910-89-4	108	X			X	
N-(2-hydroxyethyl)pyrrole (HEPyr)	6719-02-4	111	X				
N-(2-hydroxyethylimidazole) (HEI)	3699-54-5	112	X				
2-ethyl-2-methyloxazolidine	17026-89-0	115				X	
2-propyloxazolidine	53019-51-5	115				X	
N-nitroso-2-methyl-oxazolidine	39884-53-2	116	X				
5-ethyl-2-methylpyridine	104-90-5	121				X	
2-ethyl-3-methylpyrazine	15707-23-0	122				X	

Some volatile products observed in liquid phase (some pyrazines for example) were not detected in gas phase because their concentration was likely too low. Nevertheless they must be considered as potentially present in gas effluent of the pilot plant. On the other hand, several products were only observed in gas phase: 2-butanone, DMF, oxazolidine, 2-methyloxazolidine, 2-methylpyridine, 3-methylpyridine, N-nitrosodiethylamine, N-nitroso-2-methyl-oxazolidine and also acetamide, butyraldehyde, 2-ethylpyridine, 2,3-dimethylpyridine, 3-ethylpyridine, 5-ethyl-2-methylpyridine, 2-ethyl-2-methyloxazolidine and 2-propyloxazolidine only observed in stripper outlet gas. Two explanations may be considered: matrix effect can prevent their observation in liquid phase and/or they may be formed in gaseous phase. The latter may explain specific products formed in specific conditions of stripper outlet gas (high CO₂ concentration and high temperature) unless their stripping would be promoted by the higher temperature of stripper. Therefore, 38 degradation products were identified in gas phase, 17 of which for the first time, especially derivatives of pyridine and oxazolidine, 1H-pyrrole and a new nitrosamine, the N-nitroso-2-methyl-oxazolidine. 11 degradation products present in gas effluents were quantified in this work. Some aldehydes were quantified in gas effluents with the help of DNPH Sep-Pak[®] tubes. 2 tubes were used in series. Concentration profiles of these compounds in absorber outlet gas are given in Figure 8.

Figure 8. Quantification of aldehydes in absorber outlet gas.

The second tube contained some formaldehyde. Therefore, two consecutive tubes of Sep-Pak[®] with DNPH were not sufficient to retain all the formaldehyde with a flow of 6 NL/h during 1 hour. Thus, the quantification gave a minimum concentration of formaldehyde in gas effluent. Acetaldehyde was the main aldehyde detected maybe because of the even higher reactivity of formaldehyde. Propionaldehyde, likely formed from formaldehyde and acetaldehyde (Gouedard, 2014b) increased slowly and remained at a low level. In stripper outlet gas, formaldehyde, acetaldehyde and propionaldehyde were roughly one order of magnitude more concentrated than in absorber outlet gas (Table 8). Two explanations may be considered: their formation is promoted by stripper conditions and/or their stripping is promoted by the higher temperature of stripper.

Table 8: Concentrations of some aldehydes after 1600 hours in absorber and stripper outlet gases

Aldehydes concentrations in g/L at 1600 h	Absorber	Stripper
Formaldehyde	8	38
Acetaldehyde	4970	48000
Propionaldehyde	88	567

450

451 With the help of the Sep-Pak[®] DNPH tubes, it was also possible to detect the presence of butanone
 452 and butyraldehyde in the stripper outlet gas exclusively. The concentrations of butanone and
 453 butyraldehyde were both 40 µg/m³. However, neither traces of benzaldehyde nor linear carbonyl
 454 compound (from five to eight carbons) were detected.

455 At the end of the campaign, three consecutive Tenax tubes were used to make a quantitative analysis
 456 of ethyleneglycol (EG), pyrazine, 1H-pyrrole, dimethylformamide (DMF), 2-methylpyrazine (2MP), N-
 457 nitrosodimethylamine (NDMA) and diethyleneglycol (DEG) in absorber outlet gas (Table 9).

458 Table 9: Concentration of a selection of degradation products in absorber gas effluent measured on Tenax tubes

Adsorbed quantity (ng)	Molecular weight (g/mol)	Tube 1	Tube 2	Tube 3	Total	Concentration in gas (µg/m ³)
EG	62	1469	851	193	2513	419
Pyrrole	67	60	16	8	84	14
DMF	73	69	17	23	109	18
NDMA	74	1000	397	187	1584	264
Pyrazine	80	850	203	53	1106	184
2MP	94	149	0	0	149	25
DEG	106	114	57	0	171	29

459

460 For EG, pyrazine, pyrrole, NDMA and DMF, the third tube contained also these products which
 461 means that three consecutive tubes of Tenax were not sufficient to adsorb all compounds with a flow
 462 of 6 NL/h during 1 hour. However, the amount adsorbed on the third tube never exceeded 12% of
 463 the total amount except in the case of DMF. The cases of DMF and NDMA are suspicious because
 464 both of them are formed from dimethylamine. It is likely that dimethylamine reactions were still
 465 going on in the gas phase. Dettmer and Engewald reported the formation of NDMA from
 466 dimethylamine in the presence of nitrogen oxides on such tubes (Dettmer and Engewald, 2002).
 467 Therefore concentrations of DMF and NDMA might be over evaluated, especially NDMA which
 468 concentration was determined at much lower values by other techniques during the same pilot plant
 469 campaign.

470 Orbo 60 tubes were used to quantify NDMA. At the end of the campaign, the analysis of the gas
 471 effluent was done with two consecutive Orbo 60 tubes in absorber and stripper outlet gases: 75
 472 µg/Nm³ and 60 µg/Nm³ respectively. On one hand the value for absorber outlet gas confirms that
 473 value obtained with Tenax Tubes was over evaluated. On the other hand these values are one order
 474 of magnitude higher than expected values considering NDMA in equilibrium with the liquid phase
 475 (Table 10). Indeed, the concentration of NDMA measured in the solvent (Table 5) and the Henry's law

constant H of NDMA in water at 25°C (2.67×10^{-7} atm m³/mol (EPA, 2008)) enable to calculate approximately NDMA concentration in gas phase (Table 9) by using the following equation:

$$P_i = P_t y_i = H_i C_i$$

Table 10: Estimation of NDMA concentration in gas phase in equilibrium with liquid phase

Total pressure P_t (bara)	1,2	400 hours	1400 hours
y_{NDMA}	absorber	9,38E-10	1,60E-09
	stripper	7,84E-10	1,32E-09
C_{NDMA} in gas phase (µg/m ³)	absorber	3	5
	stripper	2	4

Therefore, NDMA concentration values in gas phase should be considered with caution. The Tenax tubes enabled to detect in gas phase a novel nitrosamine: the N-nitroso-2-methyl-oxazolidine (NMOx). NMOx was detected by GC/MS on three different Tenax tubes and was certainly formed by nitrosation of 2-methyloxazolidine also detected on Tenax tubes. NMOx has been synthesized and used as a standard to confirm its presence in gas effluent (Gouedard, 2014b).

Conclusion

A pilot plant campaign was performed to study MEA degradation in CO₂ capture conditions. Specific methods were developed for sampling, sample conditioning and analysis of degradation products. This analytical methodology can be adapted to the monitoring of any process with any solvent, especially the new gaseous sampling method for trace compounds identification. The analysis of the liquid phase confirmed degradation products identified in our previous works. On the other hand, gas phase analysis went further than state of art enabling identification of 17 novel degradation products. In addition to pyrazines, highlighted in our previous work, several derivatives of pyridine and oxazolidine, 1H-pyrrole and a new nitrosamine, the N-nitroso-2-methyl-oxazolidine were identified here among some others. This is a very important point because these products may be emitted to the atmosphere. Nevertheless, the knowledge of their presence enables the development of adapted counter measures to avoid any risk for environment or human health.

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