Validation of a Liquid Chromatography Tandem Mass Spectrometry Method for Targeted Degradation Compounds of Ethanolamine Used in CO 2 Capture: Application to Real Samples

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Dossier

Post Combustion CO_2 Capture
Captage de CO_2 en postcombustion

Validation of a Liquid Chromatography Tandem Mass Spectrometry Method for Targeted Degradation Compounds of Ethanolamine Used in CO_2 Capture: Application to Real Samples

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Résumé — **Validation d'une méthode de chromatographie en phase liquide couplée à la spectrométrie de masse en tandem pour des composés de dégradation ciblés de l'éthanolamine utilisée dans le captage du CO_2 : application à des échantillons réels** — Dans le domaine des émissions de gaz à effet de serre, une approche prometteuse consiste à capter et stocker le CO_2. Cependant la plupart des procédés mis en œuvre sont basés sur l'utilisation de solutions d'amines qui sont susceptibles de se dégrader et produire des composés potentiellement dangereux pour l'homme et l'environnement. Il y a donc un véritable besoin de méthodes d'analyse pour identifier et quantifier ces produits. La monoéthanolamine est choisie comme composé modèle pour les amines utilisées lors du captage du CO_2.
Une méthode de chromatographie en phase liquide couplée à la spectrométrie de masse en tandem a été développée et validée pour la quantification de six produits de dégradation de la monoéthanolamine (Glycine, N-(2-hydroxyéthyle)glycine, N-glycylglycine, bicine, N,N′-bis-(2-hydroxyéthyle) urée et diéthanolamine) qui ont été systématiquement retrouvés avec une méthode LC-MS en mode « scan » dans des échantillons réels issus de procédés de captage du CO_2 en vue de son stockage ultérieur. La principale difficulté de cette étude et son originalité se situent dans la stratégie développée pour surmonter les difficultés liées à la complexité de la matrice qui est un mélange d'eau et d'amine (70/30) : l'utilisation combinée de composés deutérés comme étalons internes et d'une approche chimiométrique récente pour valider la méthode, *i.e.* le profil d'exactitude. Pour cinq composés, il a été possible de valider la méthode avec une limite d'acceptabilité de 20 %. Cette méthode a ensuite été appliquée avec succès à l'analyse d'échantillons réels issus de pilotes et d'expériences de laboratoire.

Abstract — ***Validation of a Liquid Chromatography Tandem Mass Spectrometry Method for Targeted Degradation Compounds of Ethanolamine Used in CO_2 Capture: Application to Real Samples*** — *In the field of greenhouse gas emission, a promising approach consists in CO_2 storage and capture. However most of the processes are based on amine solutions which are likely to*

degrade and produce potentially harmful compounds. So there is a need for analytical methods to identify and quantify these products. Monoethanolamine was used as a model compound for the amines used for CO_2 capture.

A liquid chromatography tandem mass spectrometry method was developed and validated for the quantification of six products of degradation of monoethanolamine (Glycine, N-(2-hydroxyethyl) glycine, N-glycylglycine, bicine, N,N′-bis-(2-hydroxyethyl) urea (BHE Urea), and diethanolamine) that were systematically detected with a LC-MS Scan method in real samples from CO_2 capture and storage processes. The main difficulty of this study and its originality ly in the strategy developed to overcome the complexity of the matrix which is a mix of water and amine (70/30): the combined use of deuterated internal standards and a recent chemiometric approach to validate the method, i.e. *the accuracy profile. For five compounds, it was possible to validate the method with acceptance limits of 20%. This method was then successfully applied to real samples from pilot plant and lab-scale experiments.*

HIGHLIGHTS

- An analytical method based on LC/MS-MS was developed and validated using the accuracy profile;
- 6 priority compounds issued from MEA degradation were quantified in pilot plant and lab-scale experiments samples;
- Use of deuterated internal standards was found to be relevant to overcome the complexity of the matrix.

INTRODUCTION

CO_2 capture and storage is one of the promising technologies to reduce greenhouse gas emissions. To be used, this technology needs economic but also environmental acceptance. In some processes, amines are known to react with flue gas components (O_2, CO_2, NO_x, SO_x, etc.) to form degradation products, and some of them could be potentially dangerous to humans or environment according to their toxicity and their concentration. These products could be discharged to the atmosphere essentially with treated flue gas. Such amine degradation causes also amine loss, therefore additional costs, and can lead to corrosion [1], solid deposit [2] and foaming. Therefore it is necessary to list all the degradation products of amines used in CO_2 capture, to understand their formation and to study their toxicity. Alkanolamines are the most studied molecules. The benchmark molecule is MonoEthanolAmine (MEA) [3-8], but some other amines were studied: mainly DiEthanolAmine (DEA) [9-11], MethylDiEthanolAmine (MDEA) [12-14], PiperaZine (PZ) [15] and 2-Amino-2-MethylPropan-1-ol (AMP) [16]. Some alkyl amines and polyamines were studied [17-20]. The identification of amine degradation products and their mechanisms of formation were recently reviewed [21].

Amine degradation in post-combustion CO_2 capture is a main problem because of its consequences on process units and the potential impact of degradation products on environment. Therefore, amine degradation study is a key point for CO_2 capture acceptance. This is the reason why methods are required to detect, identify and quantify degradation products. DALMATIEN (Degradation of Amines in Liquid Matrix and Analysis: Toxicity or Innocuousness for ENvironment?) is an industrial research project dedicated to post-combustion. The goal of this project is to list all the degradation products of amines used in CO_2 capture, to understand their formation and to study their toxicity. A recent article [22] showed the presence of ten new degradation products (pyrazine and nine alkyl derivatives) using an analytical method based on Head Space Solid Phase Micro Extraction (HS-SPME) and Gaz Chromatograhy Mass Spectrometry (GC–MS). To go further into the analysis of degradation products, the study focused on six other compounds (Glycine, N-(2-hydroxyethyl)glycine, N-glycylglycine, bicine, N,N′-bis-(2-hydroxyethyl) urea, and diethanolamine) which were systematically detected with a LC-MS Scan method in real samples from *IFP Energies nouvelles* (IFPEN) pilot plant and lab-scale experiments. As those six compounds were considered as priority compounds by people in charge of the CO_2 capture process (IFPEN) and as most of them were not compatible with GC-MS analysis, a liquid chromatography approach had to be developed and validated to determine if they can be quantified in such a complex matrix. The use of a porous graphitic carbon column was found to be relevant in this study according to the complexity of the matrix and the high range of polarity of compounds. Validation was carried out using the total error concept and the accuracy profile which will be detailed in Section 1.4.

TABLE 1
Molecular weight, formula, retention time and MRM parameters of compounds of interest

Compound	M (g/mol)	Formula	Retention time (min)	Parent ion (m/z)	Transition (m/z)	Collision energy (eV)
MEA	61.08	C_2H_7NO	1.8	46.3	30.4*	17
DEA	105.14	$C_4H_{11}NO_2$	1.8	106.0	88.2*	11
					70.4	13
DEA-d8	113.19	$C_4H_3D_8NO_2$	1.8	114.0	96.2*	12
					78.3	15
GlyGly	132.12	$C_4H_8N_2O_3$	2.3	133.1	76.4*	8
					115.2	5
Gly	75.07	$C_2H_5NO_2$	2.3	76.2	30.6*	10
					31.6	26
Gly-d5	80.10	$C_2D_5NO_2$	2.3	78.2	32.4*	14
					33.6	32
HEGly	119.12	$C_4H_9NO_3$	2.7	120.2	74.4*	12
					56.4	19
Bicine	163.17	$C_6H_{13}NO_4$	3.7	164.1	118.2*	14
					146.2	12
BHE Urea	148.16	$C_5H_{12}N_2O_3$	17.8	149.2	62.4*	11
					44.6	19

* Transition used for quantification.

1 MATERIAL AND METHODS

1.1 Chemicals and Reagents

MonoEthanolAmine (MEA), Glycine (Gly), N-(2-HydroxyEthyl) Glycine (HEGly), N-Glycylglycine (Glygly), Bicine, Oxazolidine, Piperazine, PyraZine (PZ), N,N′-Bis-(2-HydroxyEthyl) Urea (BHE Urea), N-(2-HydroxyEthyl) EthyleneDiamine (HEEDA), N, N′-Bis-(2-HydroxyEthyl) EthyleneDiAmine (BHEEDA), DiMethylAmine (DMA), N-(2-HydroxyEthyl) ImidAzolidinone (HEIA), DiEthanolAmine (DEA) were purchased from *Sigma-Aldrich* (Saint-Quentin-Fallavier, France). DiEthanolAmine-d8 and Glycine-d5 were bought from *Eurisotop* (Saint-Aubin, France). Methanol and formic acid were purchased from *Carlo Erba Reagents* (Fontenay-sous-bois, France). Ultra pure water was produced using a Direct-Q UV 3 system (18.2 MΩ/cm) from *Millipore* (Molsheim, France).

1.2 LC-MS-MS Instrumentation and Conditions

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 (HESI-II source) (*Thermo Scientific*, Illkirch, France). It was used in positive mode, probe in position C, electrospray voltage of 2 500 V and capillary temperature of 200°C. The sheath gas was at a flow rate of 40 mL/min and the auxiliary gas at 8 mL/min. Data were acquired in MRM (Multiple Reaction Monitoring) mode with Xcalibur (Thermo software). Transitions and collision energy were optimized by infusion of each individual product (*Tab. 1*).

A Thermo HyperCarb column (PGC) 150 mm × 3 mm, 5 µm-particles (*Thermo Scientific*, Illkirch, France), an Agilent Polaris 3 Amide-C18 column 100 mm × 3 mm, 3 µm-particles (*Agilent Technologies*, Massy, France) and a Waters Symmetry shield RP18

TABLE 2
Composition of synthetic samples (concentrations given in mg/L)

Calibration	Gly	DEA	HEGly	GlyGly	BHE Urea	Bicine	DEA d8	Gly d5	MEA
Mix 1	0.2	0.2	0.5	0.01	0.5	0.02	1	1	-
Mix 2	0.5	0.5	1	0.05	1	0.05	1	1	-
Mix 3	1	1	10	0.1	5	0.1	1	1	-
Mix 4	5	5	25	0.2	10	1	1	1	-
Validation	Gly	DEA	HEGly	GlyGly	BHE Urea	Bicine	DEA d8	Gly d5	MEA
Level A	0.1	0.1	0.75	0.02	0.25	0.01	1	1	300
Level B	0.3	0.3	5	0.075	0.75	0.03	1	1	300
Level C	0.75	0.75	15	0.15	2	0.075	1	1	300
Level D	4	4	30	0.25	7	0.5	1	1	300

column 150 mm × 2.1 mm, 3.5 µm-particules (*Waters*, Saint-Quentin-en-Yvelines, France) were studied to determine the most relevant stationary phase to conduct the chromatographic separation. For both Polaris and Symmetry shield columns, the mobile phase was water with 0.1% formic acid at a flow rate of 350 µL/min. As for the PGC column, 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 350 µL/min. A prerun rinse of 100% A for 8 min was performed, then the solvent gradient started at 100% A for 0 to 10 min before being changed to 80:20 (A:B v:v) in 8 min and held for 12 min (total duration of the gradient: 30 min). 5 µL of each sample are injected. The column was at room temperature, *i.e.* 22°C maintained by the lab air conditioning system.

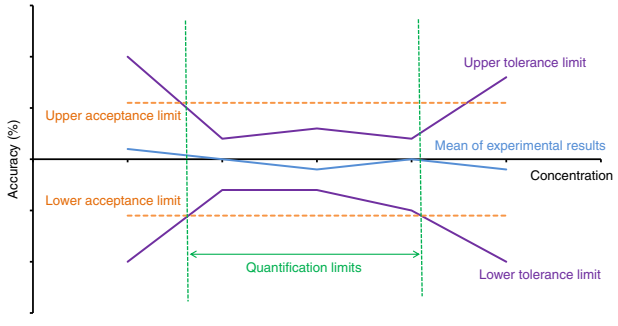

Figure 1
Example of an accuracy profile.

1.3 Sample Preparation

The range of concentration for the validation was chosen from rough estimations of their concentration in real samples using external calibration. Matrix of real samples is made of a mix water and MEA (70:30 v:v), so they are 1 000-fold diluted before injection to avoid irreversible contamination of the mass spectrometer.

Two types of samples were prepared: mix for calibration and levels for validation. The four mixes for calibration were prepared in pure water with various concentrations of the six priority compounds and deuterated Internal Standard (ISTD). Four synthetic samples, with 0.3 g/L of MEA to mimic real samples 1 000-fold diluted, were prepared with the compounds and deuterated ISTD. Table 2 provides the concentrations used for compounds and ISTD for all the samples used. Five sets of samples were prepared independently on five different days. For each one of them, preparations of calibration mix and of levels for validation were performed independently of each other.

1.4 Validation Strategy

Validation was performed using the total error concept and the accuracy profile [23-29]. This original statistical approach was successfully applied in various contexts [30-32]. For example, methods for neurotoxic l-2-amino-3-methylaminopropionic acid (BMAA) detection and quantification in complex matrix were validated

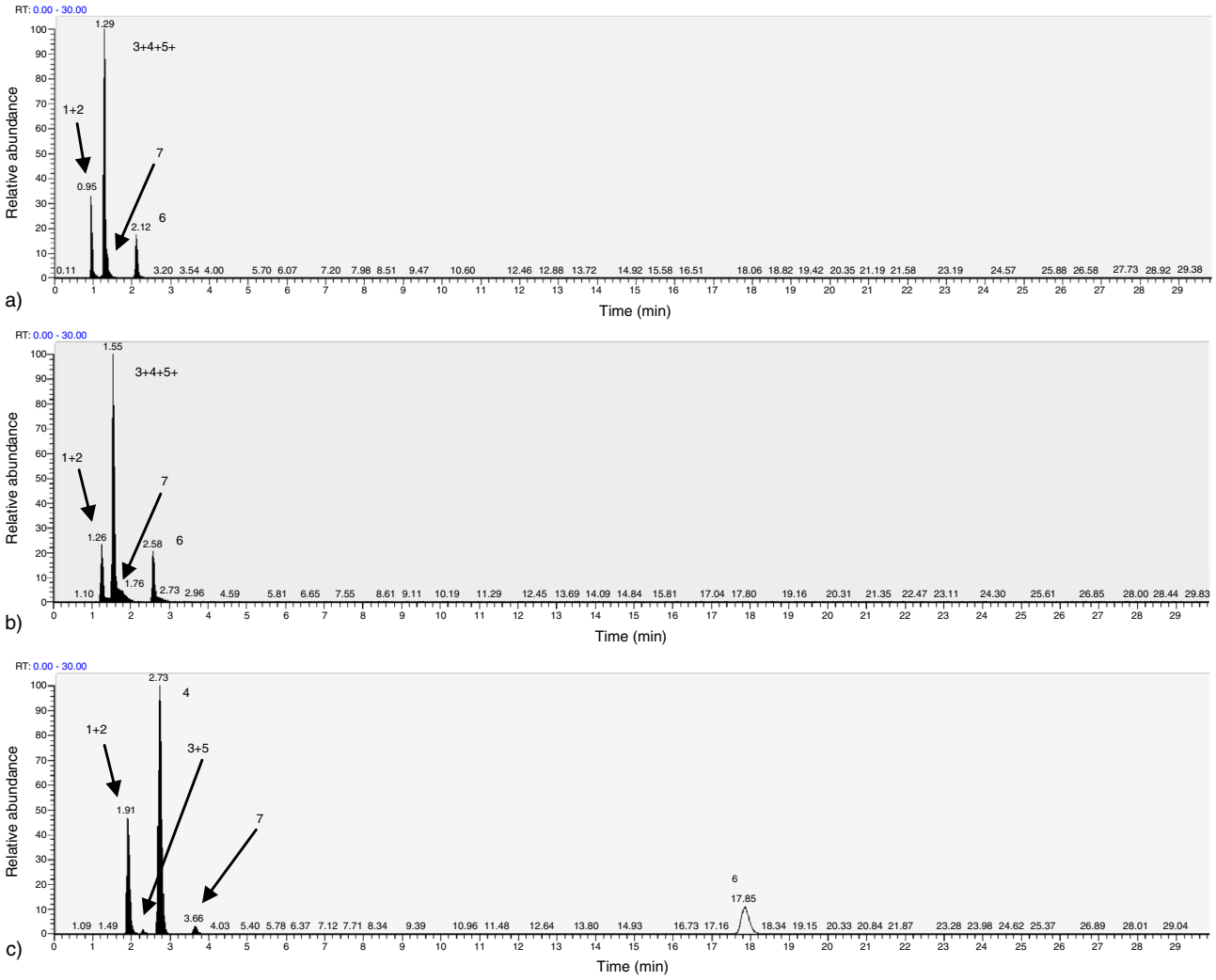

Figure 2

Comparison of chromatographic separation on a) polaris C18, b) symmetry shield RP 18, and c) PGC columns of a synthetic sample: MEA 300 mg/L, DEA 5 mg/L, Gly 5 mg/L, HEGly 25 mg/L, Glygly 0.2 mg/L, BHE Urea 10 mg/L, Bicine 1 mg/L.

using this kind of profile [33]. Those promising results on complex matrix led us to apply it to the LC/MS-MS analysis of degradation products on water/MEA matrices used for CO_2 capture and storage processes.

Validation aims at establishing, based on experimental results, if the performances of the method are compliant with its requirement. So it requires the evaluation of both the trueness and of the intermediate precision, *i.e.* the precision in the same laboratory, under different conditions (*e.g.* different days or different solvents or different apparatus or different operators). The combination of trueness and precision is called total error. In our study, the validation experiments were carried out on five series (on five different days by two different operators) and in conditions as close as possible to those that will be met during the routine analysis. Every day, new samples were prepared according to the procedure described in Section 1.3. Each sample was analyzed in triplicates using material and methods previously described. For each set of samples and each replicate, the concentration of target compounds is determined using the calibration and internal standards. Those calculated concentrations are used to know trueness and precision of measures.

The accuracy profile shows the β expectation tolerance interval of the analytical method. The upper β tolerance and the lower β tolerance calculated are both plotted at each concentration level of the validation standards and take into account their estimated intermediate standard deviation and their bias [24, 25].

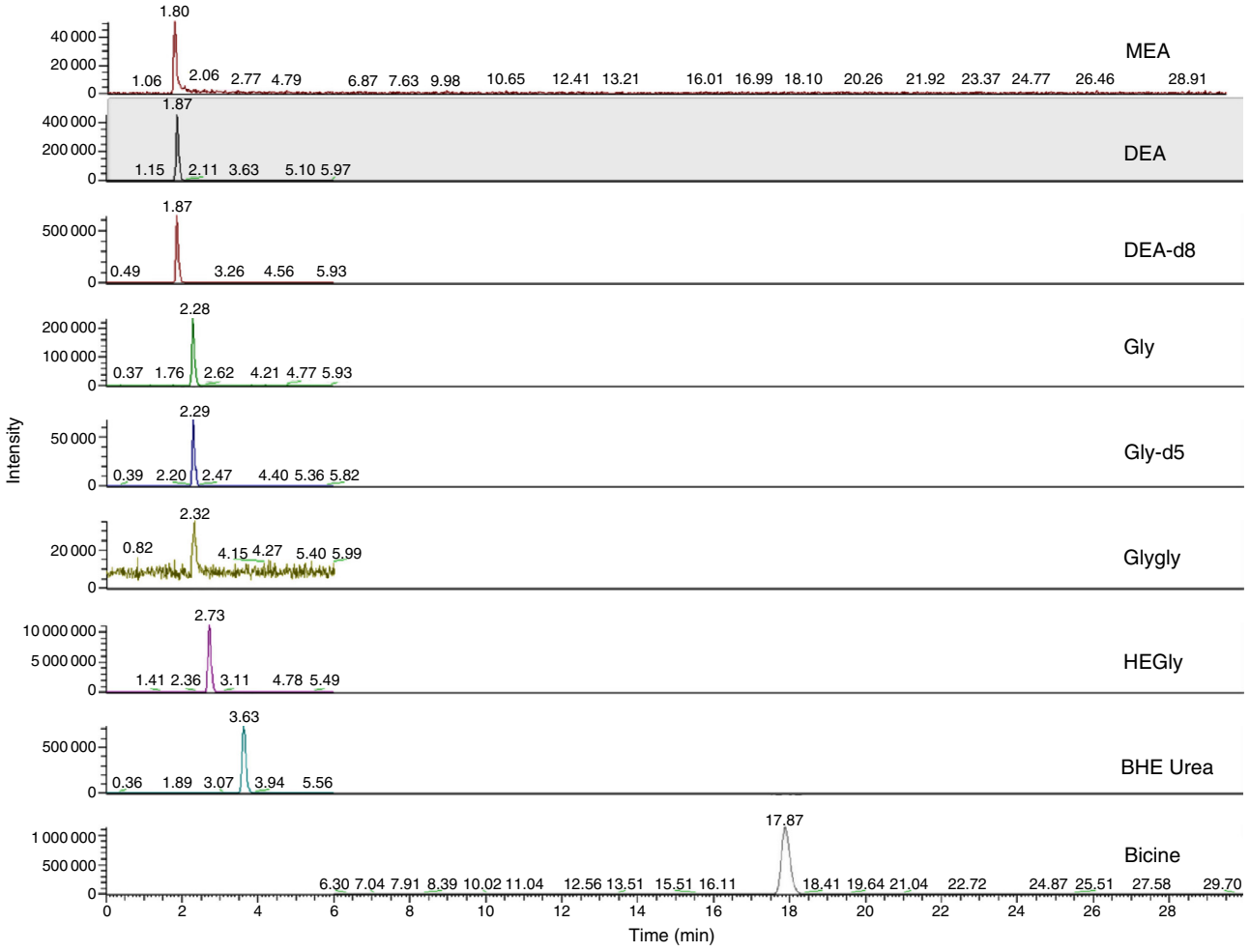

Figure 3

Chromatogram LS-ESI-MS of a synthetic sample (mix 4): MEA 10 mg/L, DEA 5 mg/L, DEA-d8 1 mg/L, Gly 5 mg/L, Gly-d5 1 mg/L, HEGly 25 mg/L, Glygly 0.2 mg/L, BHE Urea 10 mg/L, Bicine 1 mg/L – MRM transition of target compounds.

The β expectation tolerance limits were set at 80% probability level, which corresponds to an interval which will contain a future result 4 times out of 5. This graphical tool helps to define a region where each future result generated by the analytical procedure has 80% chance to fall, *i.e.* the region within four out of five future results will fall. In a word, the accuracy profile reflects directly the analytical procedure potential, and makes possible to appreciate the adequacy of different practices and to make decisions. So, the analytical method is said to be valid as long as the β interval is included between the lines representing the acceptability limits. Those limits depend on the complexity of the matrix and the study needs, in this case, and in the absence of regulatory requirements in this field, they were settled at 20% according to previous studies about quantification by LC/MS–MS [28]. Relative error (%) is plotted *versus* the concentration. The mean of experimental results give us informations about a potential bias and limits of quantification of the analytical procedure are given by the intersection of the acceptability and tolerance limits. An example of an accuracy profile is given in Figure 1.

2 RESULTS

2.1 Chromatographic Separation

As it was previously described, real liquid samples are made of a mix of water and MEA (70:30 v:v) and were

TABLE 3
Figures of merit of the validation of the LC-MS/MS method

	Concentration (mg/L)	Truness	Precision	
		Relative bias (%)	Repeatability (RSD %)*	Intermediate precision (RSD %)
DEA	0.1	0.12	2.42	15.04
	0.3	0.04	1.96	6.87
	0.75	0.02	1.22	4.29
	4	0.03	1.27	4.42
Gly	0.1	-0.07	12.23	35.49
	0.3	-0.08	8.15	11.55
	0.75	-0.09	8.00	8.09
	4	-0.06	4.49	8.20
Glygly	0.02	-0.01	24.79	27.41
	0.075	0.03	12.76	12.76
	0.15	0.05	6.11	6.11
	0.25	-0.04	4.94	10.94
HEGly	0.75	0.35	2.94	10.98
	5	0.01	1.60	4.62
	15	-0.06	2.94	7.11
	30	0.03	2.83	7.21
BHE Urea	0.25	0.63	6.35	16.06
	0.75	0.08	5.82	10.40
	2	-0.09	5.07	5.28
	7	-0.01	4.32	9.64
Bicine	0.01	0.09	17.35	47.21
	0.03	-0.28	14.21	20.57
	0.075	-0.35	9.55	9.55
	0.5	-0.24	6.06	15.20

* RSD = Relative Standard Deviation

obtained from lab-scale experiments (sample A) and pilot plant (samples B and C) at IFPEN.

Various degradation products were listed within the framework of DALMATIEN. To perform an efficient separation despite the huge diversity of physico-chemical properties of those products, three columns were tested. The Porous Graphitic Carbon (PGC) column was chosen. Indeed, its original retention mode allowed to perform a reverse phase mode analysis, keeping a higher affinity for polar compounds than frequently-used C_{18} columns where compounds are not retained enough even with 100% water (*Fig. 2*) which correspond to the smallest elution strength possible in reverse phase. Separation window is six times wider with the PGC column than with the two C_{18} ones and allows us to conduct a better separation of complex real samples. Retention of the last compound is even so strong that a gradient was necessary to maintain a reasonable analysis time with this column. Although the method could seem not optimized

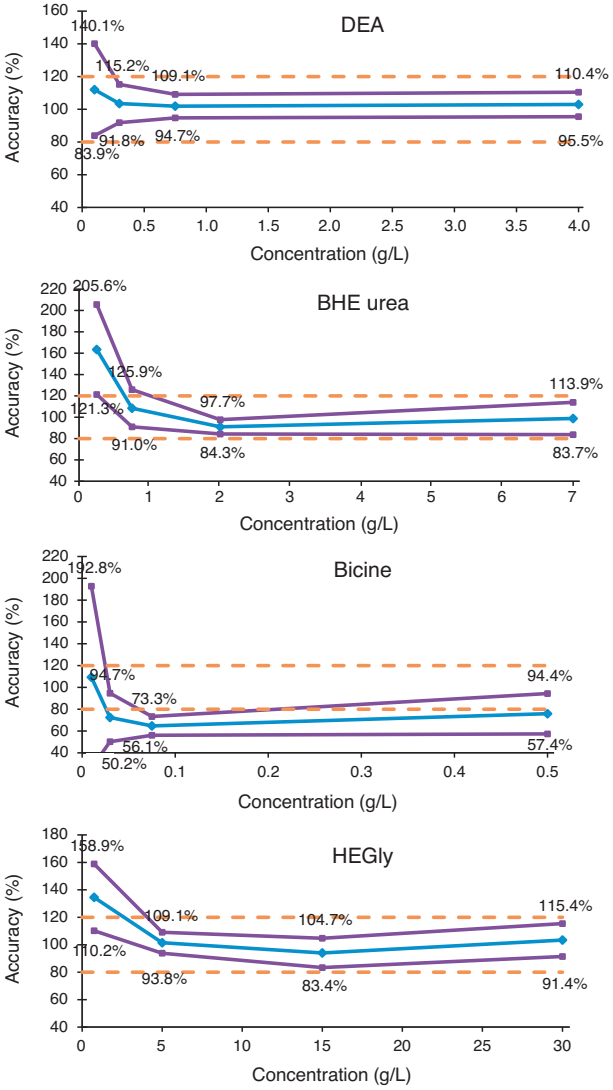

Figure 4

Accuracy profiles realized with the internal standard DEA-d8.

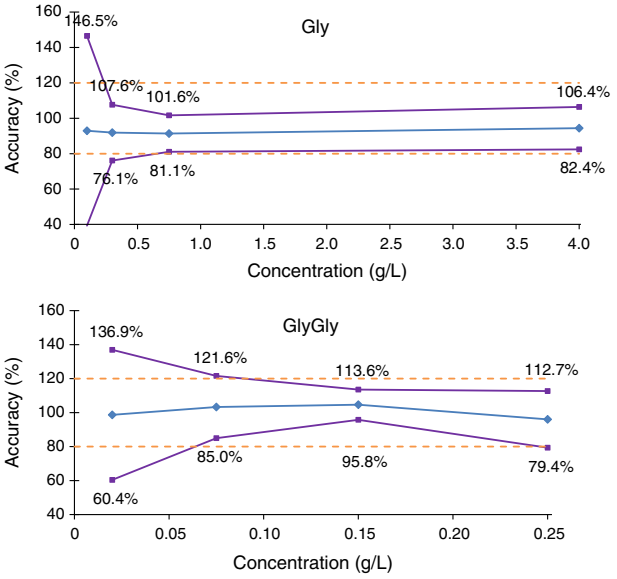

Figure 5

Accuracy profiles realized with the internal standard Gly-d5.

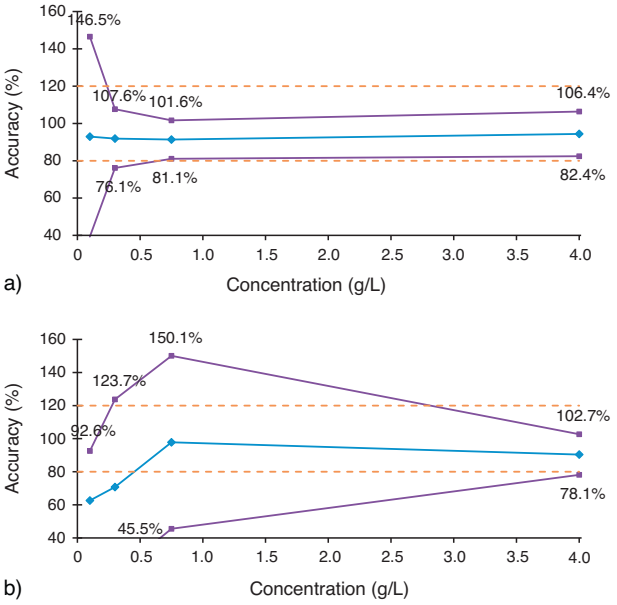

Figure 6

Comparison of accuracy profiles with a) ISTD calibration and b) external calibration for Gly.

looking at the gap between the two last eluted compounds, in fact it is. The running conditions were defined to avoid interfering compounds, present in real samples but not visible with MS-MS detection, could coelute with compound of interest and affect their ionization. Moreover, analyses can be conducted in water, at a pH between 0 and 14. This is important considering that pH of real samples is around 10. The high concentration of amine solvents raised many problems to perform analytical procedures. Samples had to be at least 1 000-fold diluted before injection to prevent the mass spectrometer from being polluted by MEA. Its retention time is 1.8 min but MEA can be detected during the whole analysis, impacting on the MS ionization recovery. And, if the concentration is too high, adducts can be even formed and pollute the device. Moreover, even with an optimized separation, most

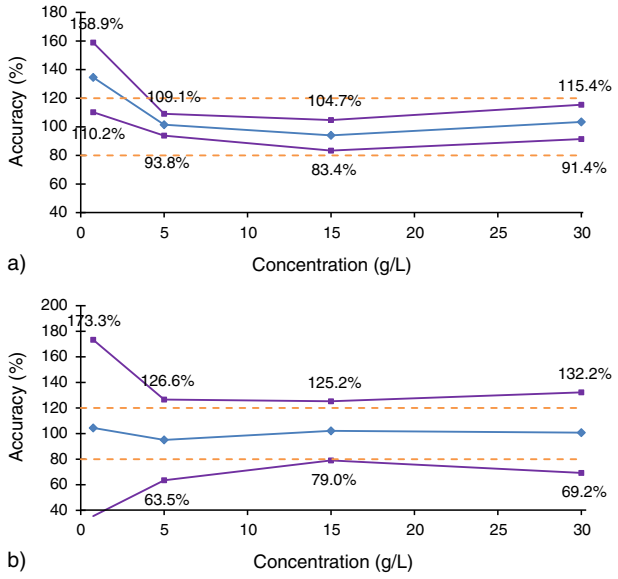

Figure 7

Comparison of accuracy profiles with a) ISTD calibration and b) external calibration for HEGly.

target compounds had a retention of less than 4 min except for BHE Urea which eluted around 18 min (*Fig. 3*). Diluting the sample allowed us to conduct analysis, but the limits of quantification are increased by 3 orders of magnitude. A compromise had to be found to get LOQ as low as possible.

2.2 Validation of the Quantification of the Six Target Compounds

Accuracy profiles were performed with concentrations calculated using deuterated ISTD DEA-d8 and Gly-d5. For each compound, two profiles were plotted, for each ISTD. Only the best one (shape, lower tolerance) was kept. Table 3 presents a recap chart of figures of merit for the validation of this LC-MS/MS method.

DEA, BHE Urea, bicine and HEGly profiles were based on DEA-d8 as illustrated by Figure 4, Gly and Glygly on Gly-d5 as illustrated by Figure 5. First thing to notice is that the method could be validated with acceptance limits set at 20% whereas, with external calibration only (without ISTD), it is impossible to reach

TABLE 4

Results of validation using accuracy profiles (concentration given in real samples before dilution)

Compounds	Validation	ISTD	Order of magnitude of limits of protection (g/L)	Valid range of concentrations (g/L)
DEA	☑ ± 20%	DEA d8	0.02	from 0.2 to 4
Glygly	☑ ± 20%	Gly d5	0.03	from 0.08 to 0.25
Gly	☑ ± 20%	Gly d5	0.2	from 0.6 to 4
HEGly	☑ ± 20%	DEA d8	0.02	from 4 to 30
Bicine	☒ bias	DEA d8	0.02	☒
BHE Urea	☑ ± 20%	DEA d8	0.05	from 1 to 7

TABLE 5

Concentration of the six target compounds in real samples from IFPEN pilot plant and lab-scale experiments

Real samples	Tolerance (%)	A (g/L)	B (g/L)	C (g/L)
DEA	± 20	0.17	0.13*	0.12*
Glygly	± 20	NF	NF	NF
HEGly	± 20	13.1	0.77*	0.8*
Gly	± 20	0.46	NQ	NF
BHE Urea	± 20	5.5	3.9	2.8

* Values out of the range of the valid concentrations, NF: not found, NQ: not quantified.

such values and the acceptance limits should be raised to 40%, which is not compliant with the present requirements! The case of Gly (*Fig. 6*) is truly relevant to demonstrate the necessity of the use of deuterated ISTD as the accuracy profile got with external calibration without ISTD is totally improper for any quantification, both the shape and the acceptance limits are not correct. DEA profile is also, not surprisingly, perfectly corrected by the use of the corresponding deuterated ISTD. Moreover, BHE Urea, HEGly (*Fig. 7*) and Glygly compounds can be validated with those ISTD, even if it is not exactly the same molecule. Results are not as good as it could have been with the correct ISTD, but this is interesting for routine analyses if only a limited number of deuterated ISTD is available to quantify various compounds.

However, for bicine profile, even if the shape is improved and the confidence interval is narrower, a bias around 30% still remains and prevents from validating this compound. A corrective factor could have been applied, but this solution may not be relevant as the matrix complexity may have some unpredictable effects. Moreover the use of any corrective factor always leads to an increase of the interval. The use of deuterated bicine seems to be the only solution to quantify properly this degradation product. Table 4 presents a recap chart for the limits of detection and the valid range of concentrations where this method can be applied for quantification. LOQ values correspond to the lower limit of the concentration range provided.

Despite a robustness study would have been beyond the scope of the present paper, it can be noticed that the success of the method validation justify *a posteriori* the good robustness of the method. Effectively the condition taken for intermediate precision, different days and operator, are quite representative of the small changes likely to occur when the method is implemented.

2.3 Application on Real Samples

This method was applied on real samples from IFPEN lab-scale experiments (sample A) and pilot plant (samples B and C). Results shown in Table 5 reveal that Glygly is under limit of detection for samples A. Otherwise, DEA, Gly, HEGly and BHE Urea concentrations can be estimated in those two real samples. Accuracy profiles were found to be relevant to determine what range of concentration was valid and to check easily if those priority compounds can be quantified in real samples. Those informations are useful to study more precisely ageing of amine solvents and dynamic of formation of degradation products. Some of them could be potentially dangerous to humans or environment according to their toxicity and their concentration.

CONCLUSION

To our knowledge, this study is the first one which presents the development and validation, based on the total error approach and the accuracy profile of an analytical method for degradation products occurring in amine based CO_2 capture process. This LC/MS method is based on a chromatographic separation conducted with a PGC column which allowed a large screening of degradation compounds. It also enabled quantification of priority compounds which were found to be relevant by specialists in charge of the CO_2 capture process. This study showed that the complexity of this kind of matrix can be partially overcome with deuterated ISTD. Acceptation limits of $\pm 20\%$ can be reached. For some compounds, it is not indispensable to use an ISTD which is the exact corresponding deuterated molecule, as it was shown for HEGly, BHE Urea and Glygly. But only validation data enabled to check if the ISTD used was relevant, and results must be cautiously interpreted as matrix effects still remain and might be sources of a non predicted increase in variability of results. Considering those promising results, this study could be pursued with other degradation products for which this LC/MS-MS method is relevant. If not, the same approach is going to be developed in GC-MS for other degradation products defined as priority compounds.

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