

# Quantitative determination of amines used in post-combustion CO<sub>2</sub> capture process by ion chromatography

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## Abstract

In post-combustion CO<sub>2</sub> capture (PCCC) with amine-based solvents, determining the amount of amine components present in the liquid phase is essential. The quantification of the solvent should be fast, accurate and simple. Towards this direction, suppressed cation exchange chromatography can be a powerful tool for the determination of the amines and their degradation products. In this paper validated methods for 12 commercial amines and 2 degradation products were developed. The amines included primary, secondary and tertiary alkanolamines, polyamines as well as cyclic amines. Amines were determined with the chromatographic system Dionex Thermo Scientific ICS-5000 with CS19 as column and CG19 as guard column. A thermoscientific conductivity detector was used for identifying the various analytes. The validated methods were used for quantitative analysis and the coefficient of determination was greater than 0.99. Moreover, applications for determination of amines from pilot plant studies, trace analysis of cationic species and analysis of degraded samples are presented. Finally, it was shown that amine concentrations can be determined fast and accurate with CS19 without any special sample preparation.

*Keywords: Amines; Ion Chromatography; CO<sub>2</sub> capture; method validation*

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## 1. Introduction

Carbon dioxide (CO<sub>2</sub>) is the major greenhouse gas emitted through human activities and the combustion of fossil fuels (coal, natural gas, and oil) is a large CO<sub>2</sub> source. The development of innovative technologies for CO<sub>2</sub> emission reduction is of great importance. In this direction, CO<sub>2</sub> capture and separation processes can be used to minimize the emissions of carbon dioxide from fossil fuel power plants. Chemical absorption using aqueous amine solutions is the most commonly used method for CO<sub>2</sub> capture from gas streams and has already reached commercial stage. Absorption using amines as solvents has been applied successfully for several decades in areas such as natural gas processing or coal gasification [1]. Various alkanolamines can be used for CO<sub>2</sub> post-combustion capture. Monoethanolamine (MEA) is often referred to as the benchmark solvent due to its good absorption properties towards CO<sub>2</sub> [2]. Furthermore, diethanolamine (DEA), promoted N-Methyldiethanolamine (MDEA), piperazine (PZ) and 2-Amino-2-methylpropanol (AMP) are among the most commonly used amines in CO<sub>2</sub> capture. Recently, several new amines and blends of amines have been proposed.

Determining the concentration of the solvent during solvent development, pilot testing as well as commercial plant operation is essential. Various amines e.g. MEA have a high degradation rate. Thus, knowing the amount of amine in the process is of high importance for controlling the amount of make-up solvent added and also to gain knowledge of solvent losses. The quantification of the solvent should be fast, accurate and simple. Ion chromatography (IC) can be a powerful tool for the determination of the amine. IC is a sub category of liquid chromatography, which is widely used for amine analysis [3]. IC can give accurate results without any special sample preparation except dilution. However, IC cannot be used for the determination of all the products of CO<sub>2</sub> absorption, e.g. carbamate.

Anion IC for amine degradation products has been used by various researchers [4-8]. Cation IC has been used from the early 90's for determination of alkanolamines using conductivity detection [9]. Kadnar [10] was the first to publish optimized methods for determination of amines used in the oil and gas industry by cation IC with the CS10 and CS12 column. Regarding PCCC research, CS17 [11] was used to determine MEA, DEA, AMP, DGA, EDA, PZ and DETA and SCS1 [12] was used for ammonium, MEA, DEA and MDEA method optimization. Method validation was performed by Wang et al. [12]. Sexton et al. [11] used a gradient method for the quantification of the above mentioned amines.

In this work, optimized validated methods are developed to determine alkanolamines, polyamines, cyclic amines and degradation products using suppressed conductivity detection. Method optimization refers to system settings i.e. suppressor set value, temperature and fast analysis time while method validation includes evaluation of the chromatographic methods with parameters such as accuracy, detection limit and quantification limit. In total, validated methods for 12 amines and 2 degradation products are presented. In addition, application of the methods for trace analyses of amines and degraded solvent analyses are shown. It is the first time that validated methods together with optimized chromatographic settings using CS19 as column for a vast variety of amines that are used in PCCC are presented.

75 **Nomenclature**

76	1,3-DAP	1,3-Diaminopropane
77	AMP	2-Amino-2-methyl-1-propanol
78	CSRS	Cationic Self-Regenerating Suppressor
79	DDI	Distilled De-Ionized
80	DEA	Diethanolamine
81	DEEA	2-(Diethylamino)ethanol
82	DETA	Diethylenetriamine
83	DGA	2-(2-aminoethoxy)ethanol
84	DIPA	Bis(2-hydroxypropyl)amine
85	DMMEA	2-Dimethylaminoethanol
86	EDA	Ethylenediamine
87	HEEDA	N-(2-Hydroxyethyl) ethylenediamine
88	IC	Ion Chromatography
89	LC-MS	Liquid Chromatography Mass Spectrometry
90	MAPA	N-Methyl-1,3-diaminopropane
91	MEA	Monoethanolamine
92	MMEA	2-(Methylamino)ethanol
93	MSA	Methanesulfonic acid
94	N-MDEA	N-Methyldiethanolamine
95	N-TBDA	N-tert-Butyldiethanolamine
96	PCCC	Post-combustion CO <sub>2</sub> capture
97	PZ	Piperazine
98	RSD	Relative Standard Deviation

## 2. Material and Methods

### 2.1 Instrumentation

Chromatographic analysis of alkanolamines was performed with a Thermo Scientific™ Dionex™ ICS-5000 system. Cations were separated with a Thermo Scientific Dionex IonPac™ CS19 analytical column (2 x 250 mm). The system was employed with a Thermo Scientific Dionex IonPac™ guard column CG19 (2 x 50mm). All sample runs were performed using both the guard and the analytical column. The guard column which is placed prior CS19 prevents sample contaminants from eluting onto the analytical column [13]. The samples were injected with a Thermo Scientific Dionex AS Autosampler. The unknown samples were carried through the CG19 guard column and through the CS19 analytical column via an eluent consisting of dilute methanesulfonic acid (MSA). The Thermo Scientific™ Dionex™ IonPac™ CS19 carboxylate-functionalized cation-exchange column is ideal for the separation of common cations, small polar amines (including many PCCC amines) using MSA as eluent. The column is packed with carboxylated resins and the various cationic species can be separated due to the variations of their affinity for the resin. CS columns have their own unique characteristics. CS12 can separate cationic species faster than the other columns while CS16 is ideal for highly concentrated samples. The latest columns of the CS series, CS17 and CS19 have the highest selectivity and they can provide the best possible separation. Furthermore, CS19 stationary phase has a higher cation exchange capacity than the CS17 [13]. CS10 can be regarded as outdated but still is being used. Dionex IonPac CS19 column supports isocratic and gradient separations of polar amines, using suppressed conductivity detection. It is the latest column of its series and has higher capacity than the Thermo Scientific Dionex IonPac CS18 column. This allows the analysis of widely disparate peak pairs and high-ionic strength matrices with less overloading of the column [13]. As suppressor, the Thermo Scientific Dionex CSRS 300 2mm (Cationic Self-Regenerating Suppressor) was used. The use of suppressor decreases the background conductivity and increases the response of the analytes. The cationic species were detected by a Thermo Scientific conductivity detector. The software that was used for all the steps of the analytical method (analyses, chromatographs, calibration plots and reports) was the Chromeleon® 7.

### 2.2 Chemicals

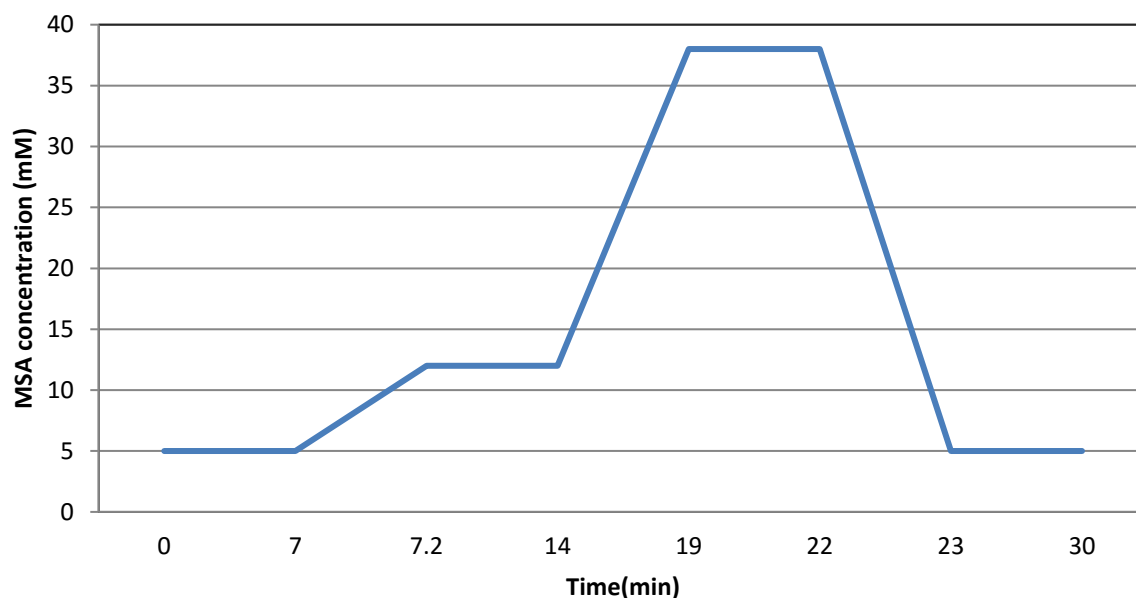
Chemicals used in this research are shown in Table 1. All the amines were purchased from Sigma-Aldrich in more than 99% purity except for MAPA, MMEA and DIPA which had purity >98% and N-TBDA with purity >97%. A 6-cation standard (lithium, sodium, ammonium, potassium, magnesium and calcium) was purchased from Thermo Scientific. The eluent that was used, methanesulfonic acid (MSA), was purchased from Sigma-Aldrich and had 99.5% purity. All the chemicals were used without further purification and all the solutions were prepared with distilled, deionized water produced by the ICW-3000 Millipore water purification system.

143 **Table 1: Short, full name, CAS and molecular formula for amines used.**

MEA	Ethanolamine	141-43-5	$\text{NH}_2\text{CH}_2\text{CH}_2\text{OH}$
N-MDEA	N-Methyldiethanolamine	105-59-9	$\text{CH}_3\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$
MAPA	N-Methyl-1,3-diaminopropane	6291-84-5	$\text{CH}_3\text{NH}(\text{CH}_2)_3\text{NH}_2$
DEA	Diethanolamine	111-42-2	$\text{HN}(\text{CH}_2\text{CH}_2\text{OH})_2$
AMP	2-Amino-2-methyl-1-propanol	124-68-5	$(\text{CH}_3)_2\text{C}(\text{NH}_2)\text{CH}_2\text{OH}$
DETA	Diethylenetriamine	111-40-0	$(\text{NH}_2\text{CH}_2\text{CH}_2)_2\text{NH}$
DEEA	2-(Diethylamino)ethanol	100-37-8	$(\text{C}_2\text{H}_5)_2\text{NCH}_2\text{CH}_2\text{OH}$
DIPA	Bis(2-hydroxypropyl) amine	110-97-4	$\text{NH}[\text{CH}_2\text{CH}(\text{OH})\text{CH}_3]_2$
PZ	Piperazine	110-85-0	$\text{C}_4\text{H}_{10}\text{N}_2$
1,3-DAP	1,3-Diaminopropane	109-76-2	$\text{NH}_2(\text{CH}_2)_3\text{NH}_2$
DMMEA	2-Dimethylaminoethanol	108-01-0	$(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{OH}$
N-TBDA	N-tert-Butyldiethanolamine	2160-93-2	$(\text{CH}_3)_3\text{CN}(\text{CH}_2\text{CH}_2\text{OH})_2$
MMEA	2-(Methylamino)ethanol	109-83-1	$\text{CH}_3\text{NHCH}_2\text{CH}_2\text{OH}$
HEEDA	N-(2-Hydroxyethyl) ethylenediamine	111-41-1	$\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{OH}$

### 146 2.3 System conditions and methods

147 Both isocratic and gradient methods were tested for the analyses. During the isocratic elution, the concentration of MSA is stable while in the gradient elution is not. Two of the optimized methods that were used for the determination of amines in aqueous solutions were isocratic methods with respectively 8mM and 20mM MSA as eluent. These methods were also validated. In addition, a gradient method with eluent concentrations from 5 to 40mM MSA was tested. With increasing eluent concentration, optimized suppressor settings were applied. The eluent gradient profile is presented in Figure 1. The isocratic method was sufficient for the detection of a single amine and amine blends with low background, stable baseline and accurate integration. The isocratic methods are much faster than the gradient method. The presented validations are based on the isocratic methods that were developed. The runtime was 15 minutes with column flow set to 0.250 mL/min and column temperature 30 °C. The suppressor current was 6mA for the 8mM MSA method and 15mA for the 20mM isocratic method. The CO<sub>2</sub> loading was found not to affect the peak shape and the amine determination; thus the methods can be used for both CO<sub>2</sub> loaded and unloaded solutions.



**Figure 1: Gradient profile of MSA. 40mM MSA corresponds to 100%.**

## 2.4 Sample and Stock Preparation

The amine stock standard solutions (2000 ppm) were prepared by diluting with distilled, deionized water (DDI water). The preparation of the standards and of the samples is based on weight per weight dilution (w/w). In order to prepare the standard solution for each amine, ~100 g of DDI water were added in an empty 1 L volumetric flask. The mass was recorded by using a Mettler Toledo scale with accuracy of three decimals. Then, 2 g of amine were put into the flask. The exact amount was recorded and afterwards DDI water was added until a total weight of 1 kg solution. The amine concentration was calculated based on the weights and the error is expected to be less than  $\pm 1\%$ . This solution is the 2000ppm amine stock and is further diluted in order to create the calibration standards. All the dilutions are made using a Mettler Toledo scale with accuracy of four decimals and the amine concentrations are calculated using the actual weights. In case of amine mix, 2 g of each amine is put into the volumetric flask. The uncertainty in the stock preparation is influenced from the accuracy of the scale. The error from the IC is mainly from the repeatability and the average relative standard deviation inside the quantification range is less than 0.5% for all amines except N-TBDA. A total error in the results is expected to be within the range of  $\pm 1.5\%$ . The range of calibration is from 10 ppm to 100 ppm in most amines. With regard to calibration curve, the curve fit type was quadratic and not linear. The evaluation of the total amount of the amines was based on the area of the peak. The vials used for all the sample preparations were made of plastic instead of glass because an unwanted peak (sodium) can be observed when using glass vials.

### 3. Results and discussion

Results from different applications are presented. First the retention times of the amines in water with the various methods that are described in this work are listed. Secondly, validation of the methods was performed in order to check the accuracy, reliability and precision of them. Finally, three method applications are presented: analysis of the degraded benchmark solvent MEA, a pilot plant mix of DEEA and MAPA solution quantification and finally the quantification of extremely low amounts of analytes.

#### 3.1 Determination of amines in aqueous solutions

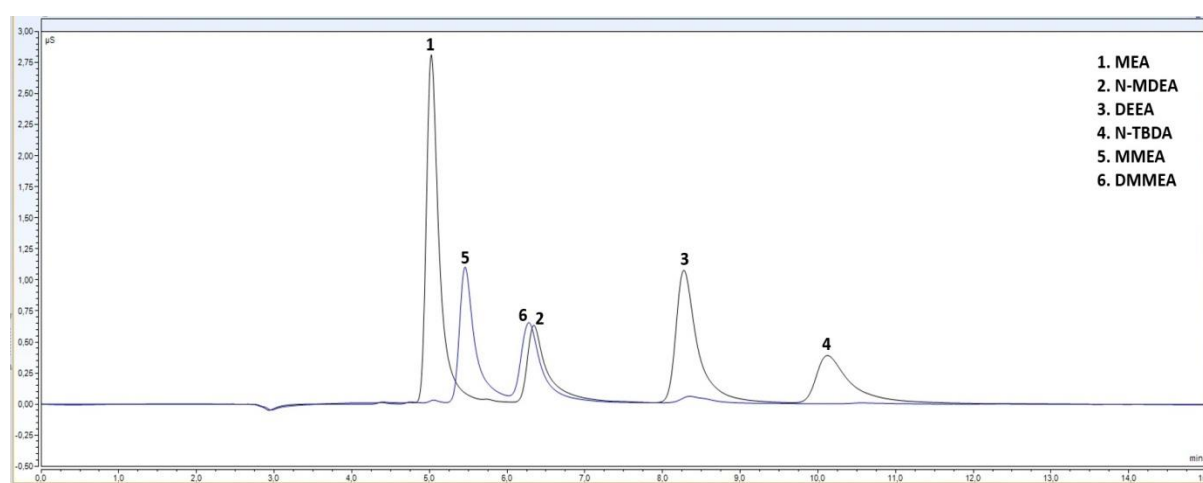
Knowing the retention times of the different amines and cations is essential for deciding the method to be used. In Table 2 a list of retention times for the various cationic species is presented. Generally, primary amines (e.g. MEA) elute first, followed by the secondary amines (e.g. DEA) and finally tertiary amines (e.g. N-MDEA). Polyamines (i.e. DETA) will elute last and only with higher MSA concentrations.

**Table 2: Retention times for amines and cations for the different methods**

Cation and Amines	RETENTION TIME (min)		
	8mM MSA	20mM MSA	Gradient method
MEA	5.1	3.8	6.6
N-MDEA	6.4	4.3	8.7
MAPA	N.E.*	8.0	22.3
DEA	5.5	4	7.2
AMP	5.4	4	7.1
HEEDA	N.E	7.3	22
DEEA	8.3	5.1	12
DIPA	6.3	4.3	8.6
Piperazine	N.E.	9.3	23.1
1,3-DAP	N.E.	6.8	21.6
DMMEA	6.6	4.4	9
N-TBDA	10.2	5.9	13.9
MMEA	5.6	4	7.4
DETA	N.E.	N.E.	25.6
Li	3.9	3.4	4.46
Na	4.4	3.59	5.30
NH <sub>4</sub>	4.8	3.73	5.89
K	5.8	4.13	7.51
Mg	8.9	4.78	13.97
Ca	11.2	4.85	14.96

N.E. : Not Eluted

If the chromatographic conditions (matrix, retention times and water purity) do not have a significant effect on the peak resolution, the isocratic method should be preferred rather than the gradient. The main reason is the faster time of analysis of the isocratic run compared to the gradient. As seen from Table 2, both the 8mM MSA and 20mM methods have shorter run times compared to the gradient one for all the amines. All the tested methods showed high accuracy and precision. On this basis, the isocratic methods were chosen for further validation. Examples of the separation of two solvent blends are shown in Figure 2. One blend contains 5 ppm of MEA, N-MDEA, DEEA, N-TBDA and the other contains 5 ppm MMEA and DMMEA. The 8mM MSA method was used. From Figure 2 it can be seen that MEA elutes first, followed by MMEA. N-MDEA and MMEA have almost similar retention times and this makes the separation difficult. DEEA is eluted after 8.3 minutes and N-TBDA elutes last after 10.2 minutes.



**Figure 2: Separation of 6 amines with CS19 and 8mM MSA as eluent.**

### 3.2 Method Validation

The analytical isocratic methods proposed were validated considering the precision, the accuracy, the limit of detection (LOD) and the limit of quantification (LOQ). The analytical range for these validations was from 10ppm to 100ppm. The coefficient of determination was higher than 0.999 for the quadratic fit of the calibration curve. Wang et al. [12] with non-suppressed conductivity detection validated methods for MEA, DEA MDEA and ammonium. The reproducibility of their standard solutions was represented by the relative standard deviation of the peak area. Their results showed high reproducibility. However, due to the fact of not using suppressor, the LOD values that were reported were higher than in this study. Non-suppressed conductivity detection leads to less sensitivity. If linear fit is the desired one, then non-suppressed conductivity should be the preferred option for analysis. The linearity for suppressed conductivity detection limits the range of analysis. Tables 3 and 4, recap the data obtained from the validation part for the analyzed amines. The shaded amines in Table 4 represent amines that can be eluted with 20mM MSA and not with 8mM.



The precision of the method is the degree of scatter between a series of measurements obtained from multiple sampling of the same homogeneous samples [14]. Precision results in Tables 3 and 4 were obtained by analyzing samples of three different concentrations, three times each. Then, the relative standard deviation was calculated. Accuracy is reported as percent recovery by the assay of known added amount of analyte in the sample [14]. The concentration covered the range of concern with concentrations close to the quantification limit, to the middle of the range and to the end of the calibration curve. For each concentration three replicates were tested. Accuracy is reported with per cent recovery and is calculated with the following equation:

$$Recovery(\%) = \frac{\bar{x}_{spiked} - \bar{x}}{x_{added}} \times 100\%$$

where  $\bar{x}_{spiked}$  is the mean result of spiked samples,  $\bar{x}$  is the mean result of the unspiked samples and  $x_{added}$  is the amount of added sample

Recovery of 100% means that the amine concentration determined with IC is the same as the true amine concentration in the sample. Recoveries that are not close to 100% indicate less accuracy. The LOD had a signal/noise ratio equal to 3-4 and the LOQ had a signal/noise ratio of 15-20. Robustness was not tested as a validation factor in this paper. Errors and biases given by these tables may be considered minimum due to weight based dilution and high suppressor effectiveness. Nevertheless, some factors such as the background effect of the conductivity detection can enhance the error. LC-MS and IC analysis were used for the quantification of the MAPA-DEEA mix. The difference in the results was less than 1% for all the samples. This can be taken as another proof that IC is capable of accurate analysis. Based on our knowledge, there is no data reported for validated methods for PCCC amines quantification with suppressed conductivity detection so far. Therefore, the results from this validation study cannot be directly compared with other studies.

**Table 3: 8mM MSA Method Validation Parameters for the various amines**

AMINES (8mM)	LOD-LOQ (ppm)		Standard Curve (Coeff. Of Determination)		Precision %RSD	Accuracy (%Recovery)
	LOD	LOQ	Linear	Quadratic		
MEA	0.01	0.05	0.9923	0.9998	0.14	100.19
N-MDEA	0.01	0.04	0.9949	0.9990	0.20	101.25
DEA	0.01	0.05	0.9910	0.9994	0.09	99.50
AMP	0.02	0.05	0.9945	0.9997	0.27	99.69
DEEA	0.01	0.05	0.9974	1.0000	0.43	102.51
DIPA	0.02	0.05	0.9951	0.9998	0.13	101.14
DMMEA	0.01	0.05	0.9949	1.0000	0.15	100.78
N-TBDA	0.02	0.1	0.9961	0.9999	0.12	98.47
MMEA	0.01	0.05	0.9955	1.0000	0.15	100.43

**Table 4: 20mM MSA Method Validation Parameters for the various amines.** The shaded amines represent amines that can be eluted with 20mM MSA and not with 8mM

AMINES (20mM)	LOD-LOQ (ppm)		Standard Curve (Coeff. Of Determination)		Precision %RSD	Accuracy (%Recovery)
	LOD	LOQ	Linear	Quadratic		
MEA	0.01	0.05	0.9945	0.9998	0.44	100.31
N-MDEA	0.1	0.3	0.9917	0.9995	0.42	101.75
MAPA	0.05	0.1	0.9911	0.9983	0.27	101.24
DEA	0.05	0.1	0.9956	0.9998	0.40	101.11
AMP	0.01	0.1	0.9988	0.9996	0.28	100.99
HEEDA	0.05	0.1	0.9977	1.0000	0.28	102.62
DEEA	0.01	0.03	0.9939	0.9995	0.33	100.80
DIPA	0.05	0.1	0.9977	0.9993	0.26	100.89
Piperazine	0.05	0.1	0.9994	0.9997	0.35	101.75
1,3-DAP	0.03	0.07	0.9999	1.0000	0.16	100.61
DMMEA	0.01	0.05	0.9939	0.9995	0.33	100.80
N-TBDA	0.1	0.4	0.9934	0.9998	0.73	99.33
MMEA	0.02	0.08	0.9959	0.9993	0.27	99.05

### 3.3 Method Applications

In this chapter applications of the different methods for the determination of amines are presented. Degraded samples, samples from pilot plant campaigns and low concentration samples are analyzed. Since MEA is the benchmark solvent at PCCC applications, a fast method for the quantification of MEA and HEEDA, which is a common thermal degradation product, would be beneficial. As for the DEEA-MAPA mixture, it started as a promising solvent for CO<sub>2</sub> capture [15] and later it was tested in pilot plants with promising results. The proposed methods also allow analysis of trace amounts of amines. During amine based PCCC, the clean gas that leaves from the top of the absorber may contain trace amount of amine. Thus, it is of great importance to quantify this amount in order to be able to control the environmental emissions and impacts.

#### 3.3.1 MEA-HEEDA

With ICS-5000 both anion and cation analysis are possible simultaneously. For degraded MEA samples, anion IC is useful for the analysis of formate, oxalate, glycolate, propionate and acetate. Cation IC can be a powerful tool for the quantification of MEA loss due to degradation and for the quantification of HEEDA. HEEDA is one of the main thermal degradation products of MEA. With 30 wt% MEA at 0.4 mol CO<sub>2</sub>/mol MEA and 120 °C for 16 weeks HEEDA formation can reach 10wt% of the whole solution [16]. The 20mM MSA method can successfully quantify HEEDA in aqueous MEA solvent. In Figure 3, the chromatogram of a sample from a 30wt% MEA thermal degradation experiment is presented. From Figure 3 it can be seen that MEA is the largest peak at a retention time of 3.8 minutes followed by HEEDA which elutes at 7.2. Davis [16], while studying thermal degradation of MEA with a Dionex ICS-2000 system equipped with a CD25 conductivity detector and an IonPac CG17 guard column with an IonPac CS17 analytical column, observed another peak which was eluted between the MEA and HEEDA. IC-MS was used and he proposed that this peak with a mass to charge ratio of 174 corresponded to the imidazolidone of the MEA trimer. However, this peak was not observed in the current thermal degradation study.

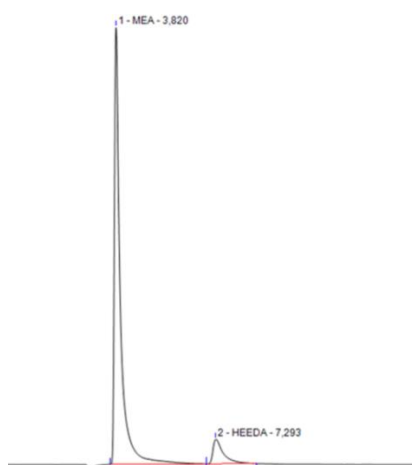
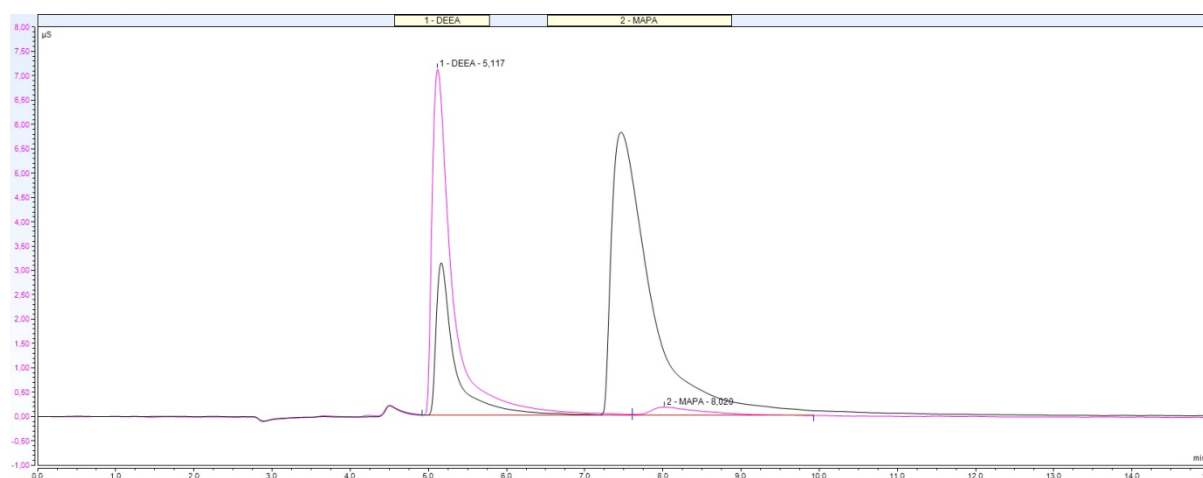


Figure 3: Degraded sample: MEA and HEEDA

### 3.3.2 MAPA-DEEA

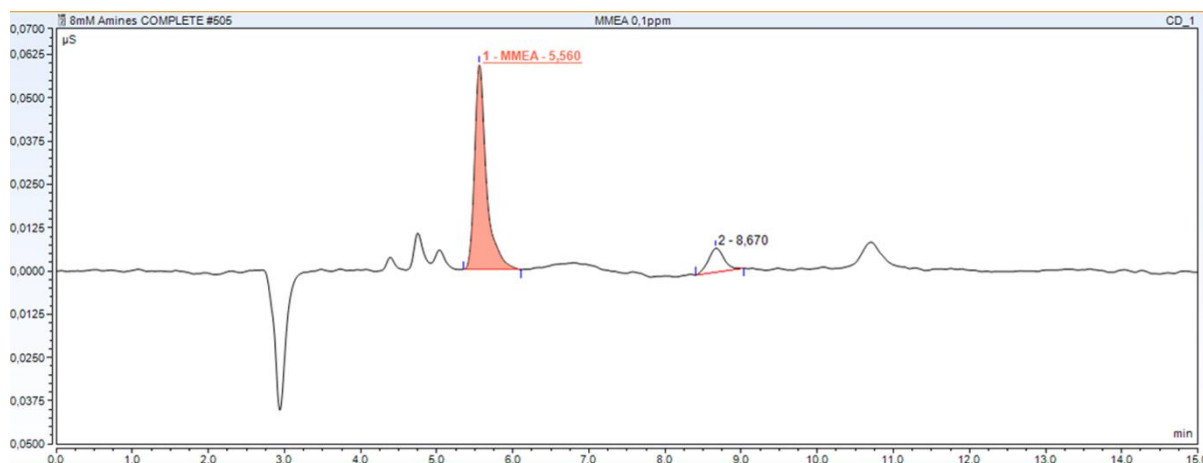
A new mixture of solvents with high potential in PCCC is the aqueous mix of DEEA and MAPA. It was tested in the Gløshaugen (NTNU/SINTEF) pilot plant and showed promising results [17]. What is very particular to this mixture is the formation of two phases, one light (almost DEEA only) and one heavy (mainly MAPA with some DEEA). The DEEA/MAPA samples were analyzed with IC [17]. Due to the vast difference in concentrations, different dilutions for the same samples were needed for the correct determination during the pilot campaign (unless a wider range is chosen for calibration). Results from LC-MS were compared with IC. The results were in good agreement. The difference between the two instruments was  $\pm 1\%$ .



**Figure 4: Determination of DEEA and MAPA samples in aqueous solutions with CS19 and 20mM MSA as eluent. The purple chromatograph is from the light phase and black one from the heavy phase.**

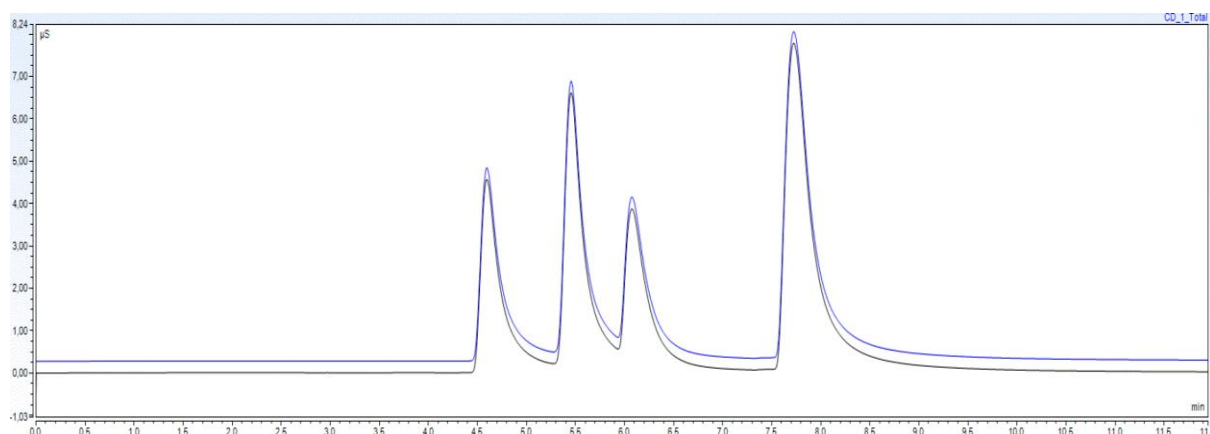
### 3.3.3 Trace analysis

The vapor pressure of amines (e.g. MEA) can cause vaporization losses from the absorber [18]. Therefore, a water wash has to be used for most systems. However, some trace amine can still be released with the gas leaving the water wash. IC can be used for both analyses of water wash solutions as well as analyses of MEA in the gas phase in connection with manual gas sampling using impingement trains where amine compounds present in the gas phase are absorbed into liquid phase [19]. The 8mM MSA method that was developed had extremely low background and can detect ppb ( $\mu\text{g/kg}$ ) of amine. In Figure 5, trace determination of MMEA is shown with the presence of other cationic species. From the figure it can be seen that MMEA concentrations as low as 0.1ppm are measured. Further determination in ppb levels is possible. The amine concentration in the gas leaving the water wash has been reported often to be in ranges of a few ppm [20] or even below 1 ppm. This indicates that IC can be used to analyze both the water wash itself as well as the gas samples withdrawn from the gas phase.



**Figure 5: Trace analysis of MMEA**

Furthermore, the optimized gradient method can separate the different cationic species while keeping the background even lower than the developed isocratic methods. In Figure 6, an example of a gradient run is shown. The background (the blue line over the chromatograph) is as low as 0.270  $\mu\text{S}$ . The only disadvantage of the gradient method is the longer analysis time for each sample. While doing trace analysis, a sodium peak from the glass vials can cause co-elution. This is why plastic vials should be used for all the dilution steps.



**Figure 6: Chromatograph with total background for the gradient method.**

## 4. Conclusions

Accurate and fast analysis is essential for amine based PCCC plants. Amines used in PCCC can be separated and determined with high precision in less than 15 minutes by cation chromatography. The state of the art CS19 column with MSA as mobile phase has a high selectivity and sensitivity for different cationic species. Trace analysis is more efficient when suppressor is used. Quadratic fit enabled a higher coefficient of determination than linear fit for the tested amines. The developed methods were able to quantify different concentrations of degraded samples accurately. In the presence of many components or of complicated sample matrixes, the optimized gradient method can separate the different cationic species while keeping the background constant at approximately 0.270  $\mu$ S. The validated methods have been used successfully for pilot plant campaigns and for thermal degradation experiments.

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