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**DEVELOPMENT OF A NEW GC-MS METHOD FOR
IDENTIFICATION AND QUANTITATIVE DETERMINATION OF AMINE
DEGRADATION BYPRODUCTS**

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ABSTRACT

A gas chromatographic technique was developed for the analysis of aqueous diethanolamine solutions and their degradation products. The Lean DEA and MDEA and the rich DEA/MDEA samples are taken from fresh amine solutions in absorption units and desorption units of Fajre-jam gas refinery respectively. The technique consisted of extracting organic phase by means of a mixed solvent, (isopropyl alcohol-ethyl acetate (1:5)) instead of the conventional alcohol solvents. Ethyl acetate increases the extraction efficiency by reducing solubility of degradation by products in water. Prepared solutions are mixed with a derivatization reagent (N,o-Bis,Trimethylsilyl, trifluoroacetamide) BSTFA. BSTFA by reacting with their OH groups and elimination of hydrogen bonds in amine degradation by products, transform these compounds to their volatile derivatives and increases selectivity of the stationary phase. The results showed that with optimizing the extraction, number of components and precision in their retention time detection by GC-MS method increases significantly.

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INTRODUCTION

Most sour gas processing facilities use chemical absorption using alkanolamines (or amines in short) to separate hydrogen sulfide and carbon dioxide from the raw gas. The alkanolamines of prime significance include monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA) and activated methyldiethanolamine (a-MDEA)[1]. Normally the amine processes are cycles of absorption and desorption in order to permit the reuse of the absorbent. Due to the closed loop nature of these processes, non-regenerable contaminants such as amine degradation products, heat stable salts, heavy hydrocarbons and particulates tend to accumulate and can cause major reduction in efficiencies and operational problems. Contaminants in amine solutions can arise from various sources and usually exist in several different forms.

Although the acid gas-amine reactions are reversible, irreversible reactions may also occur, resulting in products from which the amines are not easily recovered. This phenomenon is called degradation [2].

Amine degradation has two main causes: first, flue gases contain CO₂, O₂, and in a smaller amount, some NO_x and SO_x, and second, high temperature is achieved in the stripper (around 120 °C for MEA). Thus, amines are subject to three types of degradation: thermal degradation, degradation due to CO₂, and oxidative degradation. Because of their interest in natural gas treatment and in postcombustion applications, alkanolamines degradation has been studied for quite some time.

Since the 1950s, MEA stability has been investigated at stripper conditions or with the presence of oxygen [3-7]. Other authors also reported its degradation in a real CO₂ capture facility [8]. Furthermore, numerous studies concerning diethanolamine (DEA) [9-16] or N-methyldiethanolamine (MDEA) [16-20] degradation with temperature or in the presence of gas (CO₂ and/or O₂) are described in the literature.

The degradation rate (particularly the CO₂ induced degradation) depends on the chemical structure of the amines and the plant operating conditions.

The presence of oxygen in the sour gas streams or treating solutions may cause oxidative degradation and lead to the production of organic acids. The presence of some anionic species and/or stronger acids (as compared with hydrogen sulfide and carbon dioxide) in the raw feed gas to amine plants, leads to the formation of amine salts from which amine is not recoverable through steam stripping process. The amine salts are called heat stable salts and both organic and inorganic salts may occur. The inorganic salts such as chloride, sulfate and phosphates typically are found in produced or cooling waters. Sulfate and thiosulfates and cyanates can also be formed by reaction between oxygen and H₂S and cyanic acid and H₂S, which are more prevalent in petroleum refinery gases.

The issue of degradation induced by the presence of sulfur, polysulfides and carbon monoxide is a subject that gas refiners have been dealing with during the past few years.

In addition to the Non volatile Contaminants and Suspended solids, other contaminants may exist in the amine solutions such as anti-foaming agents, sealants, lubricants and corrosion inhibitors. Despite their low concentration in amine solutions, they may accumulate over time and affect the overall solution efficiency and plant performance.

In order to understand the behavior of contaminated amines, the impurities and their concentrations must be known. As the amine solutions become contaminated, they lose their effectiveness and cause operational problems, which can lead to plant shutdowns. Depending on the type of impurities, problems such as Reduction in Solution Capacity and Gas Plant Performance, Foaming, Fouling and Corrosion may arise.

All of the methods for analyzing aqueous amine solutions, such as IC, and GC-MS have some difficulties and none of them can analyze all of the components in the solution. In the present work, significant advances have been made on sample preparation in a GC method to analyze acid gases, hydrocarbons, water, amine and degradation products content of aqueous amine solutions.

In GC-MS method, one of the major problems is extraction of amine and degradation products from aqueous solution. In common methods, an alcohol is used for this aim and because of high solubility of alcohols in water, some of pollutants main in the water and missed. For optimizing of this extraction, we have used a mixture of isopropyl alcohol- ethyl acetate (1:5) solution as extractor solvent and a derivatization reagent (N,o-Bis,Trimethylsilyl, trifluoroacetamide) BSTFA.

Fajre-jam gas refinery is 2th big refinery with eight Amine sweetening unit in Iran. It uses diverse Alkanoamines as DEA, MDEA, DEA/MDEA and aMDEA in its units. The aim of this work was to investigate amine degradation products in it's Amin samples taken from desorption columns.

MATERIALS AND METHODS

Lean DEA and MDEA samples are taken from fresh amine solutions in absorption unites and the rich DEA/MDEA samples are taken from desorption unites. Water content of Amine aqueous solutions are shown in table1.

Amine	Type	Amine content
DEA	Lean	30%
MDEA	Lean	45%
DEA/MDEA	Rich	20% / 25%

Table1. Specification of Amine samples

Helium gas with 99.99% was used as carrier gas. Potassium hydroxide salt (for water removing from solutions) with 99% purity, isopropyl alcohol and ethyl acetate solvents were purchased from Merk and BSTFA is purchased from Sigma- Aldrich. A GC-MS equipment from Agilent Technologies Company (model N6890) with Willey7 data processor is used.

Specification of GC/MS is shown in table2.

part	specification	part	specification
Column	HP-5	Oven ramp	10 C· min ⁻¹
Length	30 m	Final temp.	320 C
Internal diameter	25 mm	Flow rate (constant)	1 mLmin ⁻¹
Thickness	0.1 μm	Injector temp.	250 C
Initial temp.	50 C	Detector temp. (MS Source)	230 °C
Initial hold time	0.5 min	Detector temp. (MS Quad)	150 °C

Table2. Specifications of the GC/MS System

Sample preparation

With chemical reaction we can transform compounds to their volatile derivatives and Silicate hydroxyl, carboxylic acid, Amine, thionic and phosphate groups.

BSTFA increases their volatility by reacting with their OH groups. With elimination of hydrogen bounds in amine degradation by products, these compounds transform to their volatile derivatives and selectivity of the stationary phase increases. Fig1 shows Mechanism of BSTFA (derivatization reagent) reaction with sample hydroxyl groups.

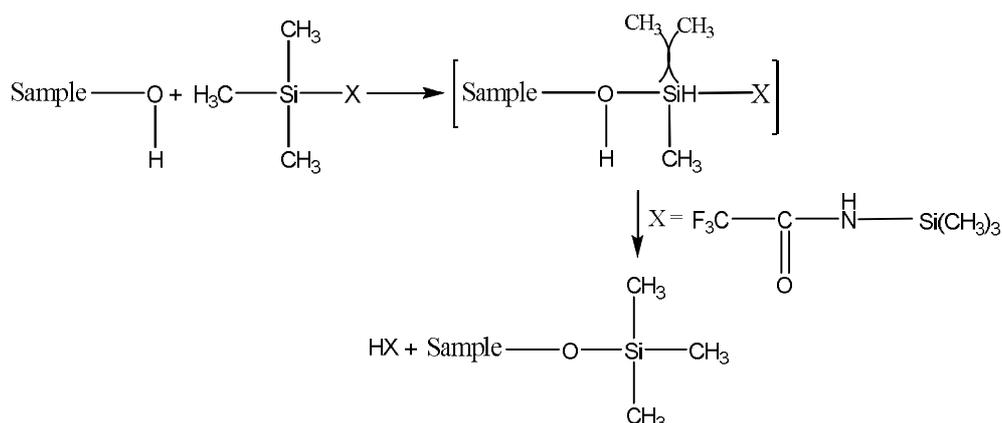
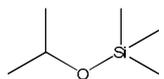
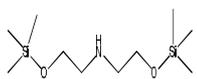
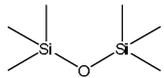
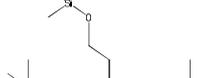
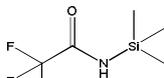
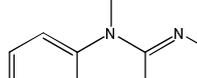
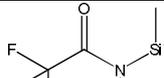
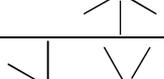
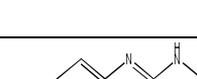
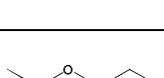


Figure1. Mechanism of BSTFA (derivatization reagent) reaction with sample hydroxyl groups

In the first method, we add Potassium hydroxide salt to 1mL of Amine solution until saturation state and then by adding 3mL solvent (isopropyl alcohol) to the solution, extract organic phase from aqueous one. After evaporating the solvents we add 250 μ l BSTFA (65°C) to the solution and leave it for 30 minutes until derivetization complete. Then we inject 1 μ l of this solution to the GC-MS. In the second method we repeat the previous method with the modified solvent (isopropyl alcohol- ethyl acetate (1:5)).

Ethyl acetate increases the extraction efficiency by reducing solubility of degradation by products in water.

The results of analysis for Lean DEA solutions with two methods are shown in table 3, 4.

structure	Silicate compound	R.t.	structure	Silicate compound	R.t.
	Silane, trimethyl (1-methylethoxy)	1.46		Bis(trimethylsilyl)ethane diethanolamine	12.24
	disiloxane, hexamethyl	1.55		Silane, nitrotris(ethyleneoxy)tris(trimethyl)	12.40
	acetamide, 2,2,2-trifluoro-n-(trimethylsilyl)	1.87		10-methylpyrazino[2,3-b][1,4]benzothiazine	13.46
	acetamide, 2,2,2-trifluoro-n,n-bis(trimethylsilyl)	2.61	-	-	15.45*
	trisiloxane, octamethyl	2.93		7-methoxy-1,4,6-triazaphenothiazine	15.92*
	2-bis(trimethylsilyloxy)ethane	4.08	-	-	15.16*

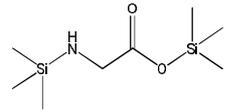
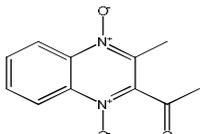
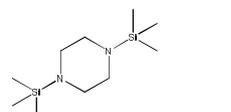
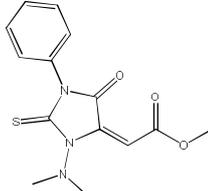
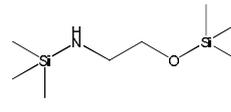
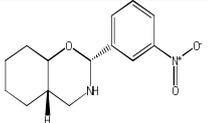
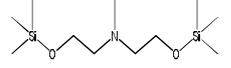
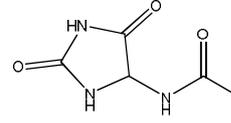
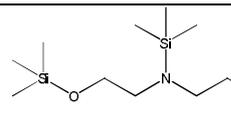
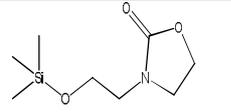
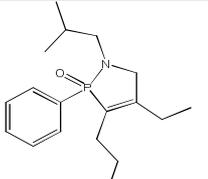
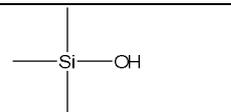
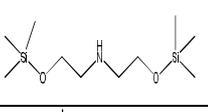
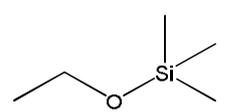
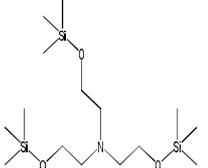
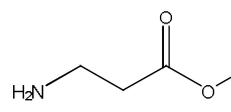
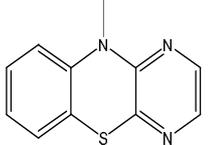
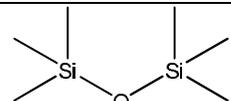
	Glicine, n-(trimethylsilyl)-trimethylsilyl ester	4.65		2-methyl-3-acetyl-quinoxaline 1,4-dioxide	17.04
	Piperazine, 1,4-bis(trimethylsilyl)	7.19		1-phenyl-3-dimethylamino-4-methoxy carbonylmethylene-perhydro-5-oxo-2-thioxoimidazole	18.24
	1,2-bis(trimethylsilyloxy)ethane	8.16		2H-1,3-Benzoxazine, Octahydro-2-(3-Nitrophenyl)-trans	19.48
	Methanamine, n,n-di(2-trimethylsilyloxyethyl)	8.49	-	-	20.38*
	allantoin	8.76	-	-	20.55*
	Silanamine, 1,1,1-trimethyl-n,n-bis[2-(trimethylsilyloxy)ethyl]	10.25	-	-	21*
	3-(2-trimethylsilyloxyethyl)-2-oxazolidinone	10.85		1-isobutyl-4-ethyl-2-phenyl-3-propyl-1,2-azaphospholen-2-oxide	23.99

Table3. Lean DEA GC-MS analysis with Isopropyl alcohol and BSTFA

structure	Silicate compound	R.t.	structure	Silicate compound	R.t.
	Silane, trimethyl	1.31		Bis(trimethylsilyl)ether of diethanolamine	12.22
	Silane, ethoxytrimethyl	1.38		Silane, nitrilotris(ethyleneoxy)tris(trimethyl)	12.42
	beta-alanine, trimethylsilylester	1.46		10-methylpyrazino[2,3-b][1,4]benzothiazine	13.46
	disiloxane, hexamethyl	1.51	-	-	15.48

	acetamide,2,2,2-trifluoro-n,n-bis(trimethylsilyl)	2.09		7-methoxy-1,4,6-triazaphenothiazine	15.92
	trisiloxane, octamethyl	2.93	-	-	16.56*
	1,2-bis(trimethylsiloxy)ethane	4.07		Silanamine,1,1,1-trimethyl-n,n-bis(trimethylsilyl)	16.99
	Glicine, n-(trimethylsilyl)-trimethylsilyl ester	4.64		1-phenyl-3-dimethylamino-4-methoxy carbonylmethylene-perhydro-5-oxo-2-thioxoimidazole	18.28
	Propanoic acid, 2-(methoxyimino)-trimethylsilyl ester	4.99		2h-1,3-benzoxazine, octahydro-2-(3-nitrophenyl)-trans	19.48
	1,2-bis(trimethylsiloxy)ethane	8.20	-	-	20.38*
	Methanamine, n,n-di(2-trimethylsilyloxyethyl)	8.51	-	-	20.55*
	allantoin	8.76	-	-	21.02*
	Bis(trimethylsiloxy)thiodiglycol	10.06		1, isobutyl-4-ethyl-2-phenyl-3-propyl-1,2-azaphospholen-2-oxide	23.99
	Silanamine,1,1,1-trimethyl-n,n-bis[2-trimethylsilyl]oxy]ethyl	10.25			

Table4. Lean DEA GC-MS analysis with Isopropyl alcohol+ ethyl acetate and BSTFA

In this tables, polymeric compounds resulted from amin degradation (THEED, TEHEED,...) have different Retention times but they have similar mass spectra .thus, mass spectra for retention times 15.48, 16.56, 20.38, 20.55, 21 are related to THEED, TEHEED and their other polymeric derivatives.

Results showed that in all of lean DEA, MDEA and mixed DEA-MDEA rich samples taken from sweetening units of jam refinery; this method increased the number of components and precision in their retention time detection by GC-MS method significantly.

CONCLUSION

In this work we analyzed degradation products of Alkanoamines by GC-MS and with new extraction method. The result showed that in all of MDEA and mixed DEA-MDEA solutions, this method with optimizing the extraction, increased the number of components and precision in their retention time detection by GC-MS method significantly.

REFERENCES

1. Dawodu O.F., and Meisen A. (1996). Degradation of Aqueous Diethanolamine Solutions by Carbon Disulfide", *Ibid*, 10(1):1
2. Dawodu O. F., and Meisen A. (1994). Mechanism and Kinetics of COS-induced Diethanolamine Degradation", *Ind. Eng. Chem. Res.*, 33(3):480
3. Chi, S.; Rochelle, G. T. (2002). Oxidative Degradation of Monoethanolamine. *Ind. Eng. Chem. Res.*, 41: 4178
4. Goff, G. S.; Rochelle, G. T. (2004). Monoethanolamine Degradation: O₂ Mass Transfer Effects under CO₂ Capture Conditions. *Ind. Eng. Chem. Res.*, 43: 6400.
5. Goff, G. S. (2005.). Oxidative degradation of aqueous monoethanolamine in CO₂ capture processes: iron and copper catalysis, inhibition, and O₂ mass transfer. Ph.D. thesis, University of Texas, Austin
6. Sexton, A. J., Rochelle, G. T. (2009). Catalysts and Inhibitors for MEA oxidation. *Energy Procedia*, 1: 1179.
7. Supap, T., Idem, R. O. (2006). Tontiwachwuthikul, P., Saiwan, C. Analysis of monoethanolamine and its Oxidative Degradation Products during CO₂ Absorption from Flue Gases: A Comparative Study of GC-MS, HPLCRID, and CE-DAD Analytical Techniques and Possible Optimum Combinations. *Ind. Eng. Chem. Res.*, 45: 2437
8. Strazisar, B. R., Anderson, R. R., White, C. M. (2003). Degradation Pathways for Monoethanolamine in a CO₂ Capture Facility. *Energy Fuels*, 17: 1034
9. Kennard, M. L., Meisen, A. (1980). Control DEA Degradation. *Hydrocarbon Process., Int. Ed.* 59: 103
10. Meisen, A., Kennard, M. L. (1982). DEA Degradation Mechanism. *Hydrocarbon Process., Int. Ed.* 61: 105
11. Kennard, M. L.; Meisen, A. (1983). Gas Chromatographic Technique for Analyzing Partially Degraded Diethanolamine Solutions. *J. Chromatogr.* 267: 373
12. Kennard, M. L., Meisen, A. (1985). Mechanisms and Kinetics of Diethanolamine Degradation. *Ind. Eng. Chem. Fundam.*, 24: 129
13. Kim, C. J.; Sartori, G. (1984). Kinetics and Mechanism of Diethanolamine Degradation in Aqueous Solutions Containing Carbon Dioxide. *Int. J. Chem. Kinet.*, 16:1257
14. Hsu, C. S., Kim, C. J. (1985). Diethanolamine (DEA) Degradation under Gas-Treating Conditions. *Ind. Eng. Chem. Prod. Res. DeV.* 24: 630
15. Holub, P. E., Critchfield, J. E., Su, W.-Y. (1998). Amine Degradation Chemistry in CO₂ Service. 48th Annual Laurance Reid Gas Conditioning Conference, Norman, OK, March 1-4:146
16. Dawodu, O. F., Meisen, A. (1996). Degradation of Alkanolamine Blends by Carbon Dioxide. *Can. J. Chem. Eng.*, 74: 960
17. Chakma, A., Meisen, A. (1997). Methyl-diethanolamine Degradation - Mechanism and Kinetics. *Can. J. Chem. Eng.*, 75: 861.
18. Ye, Q., Zhang, S. (2001). Methyl-diethanolamine Degradation Products in Desulphurization Process for Acidity Waste Gas. *Gaoxiao Huaxue Gongcheng Xuebao*, 15:35
19. Chakma, A., Meisen, A. (1988). Identification of Methyl-diethanolamine Degradation Products by Gas Chromatography and Gas Chromatography - Mass Spectrometry. *J. Chromatogr.*, 457:287

20. Clark, P. D., Dowling, N. I., Davis, P. M. (2004). Introduction to Sulphur Chemistry and Sulphur Handling, Sulphur 2004 Conference, Barcelona, Spain, October 24, British Sulphur Publishing: London, England.