Analysis of Amine Solutions by Gas Chromatography

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ABSTRACT

Currently, the most common method to analyze for acid gases in amine solutions is by wet chemistry titration which is both tedious and time consuming. A simple gas chromatographic method now exists which is accurate and performs one analysis within eight minutes.

INTRODUCTION

As energy prices continue to escalate, the performance and efficiency of all gas processing equipment becomes of critical importance. In many cases, performance evaluations are quite difficult due to the lack of convenient analytical procedures. This is especially true for amine gas sweetening units where measurement of the acid gas and hydrocarbon content of the aqueous amine solution is both problematic and time consuming.

Currently, the most popular analytical method for determining the acid gas concentration in aqueous amine solution employs a wet chemistry titration. In the method for CO_2, the amine sample is mixed with an excess of standard base and heated to boiling. Since the amine/acid gas complex is thermally unstable, the acid gas is converted into an ionic species and is precipitated by an appropriate metal salt. The filtrate is titrated with a standard acid to determine the concentration of uncarbonated amine in the sample. Bromocresol green, cresol red and phenolpthalein are commonly used to indicate the end points [3,4,6 and 7].

The total amine in the solution is usually determined by titrating the liquid sample with a standard acid in the presence of an indicator. Bromophenol blue, methyl orange and methyl red are used to indicate the end point in this titration [5,6,8]. The CO_2 content of the solution is calculated as the difference between the total amine and the uncarbonated amine assuming a 1:1 stoichiometry between the amine and CO_2 [11]. Hikita et al. (1977) [6] has verified this stoichiometric ratio for the tertiary amine TEA.

The water content is most often determined by the Kieselbach Modification of the Karl Fischer method [5]. The end point is determined by an electronic detector and the method is applicable over wide ranges of water concentrations.

The wet chemistry titration has a number of serious disadvantages. The total time required for an experienced technician to analyze one carbonated amine solution could be as long as 1-1/2 hours. During part of this time, the CO_2/amine solution is open to the atmosphere so both flashing of CO_2 and degradation of the amine can occur.

Several problems are also encountered when attempting to sample amine solution streams under pressure.

Obviously, significant flashing will occur in most cases when the pressure is released on rich amine solutions. Freshly prepared solutions of standardized acid and base must also be available and verified daily before use. Blank runs should also be made to properly execute the titration. The solution analysis by titration is often complicated by the presence of impurities and degradation products. Some of the degradation products cannot react with the acid gases but are titrated as carbonated amine. Other degradation products are heat stable salts which are also titrated as free amine [1]. Most chemical methods of ethanolamine analysis depend on amine functionality and are often nonspecific and inaccurate [2].

Wisniewski (1961) [12] devised a GC technique which could analyze for amines on one column and the acid gases and H_2O on another column but could not analyze for all components with a single sample injection. When analyzing for the acid gases and H_2O, the column was pretreated with an injection of HCl. The HCl scrubbed the amine from the sample and allowed the acid gases and H_2O to elute for analysis. The saturation of the column with amine made reproducibility difficult.

All of the above methods for analyzing aqueous amine solutions have one or more major difficulties and none of the methods can analyze for all of the components in the solution. In the present work, significant advances have been made on a GC method to analyze for acid gases, hydrocarbons, water and amine content of aqueous amine solutions.

DEVELOPMENT OF THE GC METHOD

In developing the GC method, several problems were anticipated. First, ethanolamines are very reactive compounds. The polar hydroxyl and amine groups have a strong adsorption affinity for silaceous column supports. The success of a stationary liquid support was improbable due to the strong physicochemical interactions and slow diffusion of the amines through the liquids. However, Saha et al. (1977) [10] have shown that a short column with Tenax-GC packing can be used to analyze MEA, DEA, TEA and their impurities. Sharp distinct peaks with good separation were obtained in less than 8 minutes using a Perkin-Elmer model 900 gas chromatograph with a flame ionization detector. Tenax-GC is an organic polymer bead with a very weakly interacting surface permitting rapid mass transfer, fast elution and sharp peaks and is reported to have excellent thermal stability [9].

A second potential problem was the formation of thermal degradation products at high column temperatures in the GC. However, Saha et al. (1977) [10] reported that alkanolamines do not undergo rapid thermal decomposition at injection port temperatures up to 375°C. The degradation of amines is probably more a function of time than of temperature. In a GC, the time spent on the columns is very short so degradation is insignificant.

A third problem with analyzing the components in amine solutions was their tremendous range of boiling points from -80°C for CO_2 to 250°C for MDEA. Thus an isothermal column oven could not be used and a rapid temperature program was needed for a short elution time. A high injection port temperature would be required to vaporize the sample. Furthermore, a flame ionization detector would not be satisfactory since H_2O and CO_2 are not combustible.

Column Configuration:

With the above guidelines in mind, a GC was chosen with temperature programming capability, a thermal conductivity detector and molecular sieve as the reference column. The carrier gas was helium at a flow rate of 40 ml/min. The GC was a Shimadzu GC-8A with a Shimadzu model C-RIB integrator. The Shimadzu GC was first configured with a single Tenax-GC column. An injection port temperature of 270°C and a temperature program of 20°C per minute was used to investigate the column capabilities.

Unfortunately, the Tenax-GC column alone was incapable of producing a separation between the light components (H_2S, CO_2, H_2O, C_1, C_2, etc). To separate the light components, a simple column switching device with two columns in series was constructed. The first column containing Tenax-GC was designed to give good separation between the amine and light components. The second column containing Poropak Q was designed to

separate the light components. Poropak Q is an ethylvinylbenzene-divinylbenzene copolymer that is cross-linked and can withstand temperatures to at least 250ºC before polymer degradation occurs. The pressure drop across the Poropak Q column was balanced with a restrictor valve. Both columns were purchased prepacked from Alltech Associates. The column arrangement is shown in Figure 1.
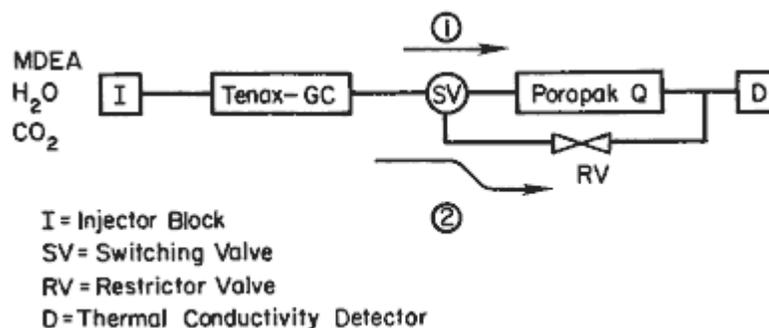

I = Injector Block
SV = Switching Valve
RV = Restrictor Valve
D = Thermal Conductivity Detector

Figure 1. GC column configuration.

After injection, the sample vaporized and the light components flowed rapidly through the Tenax-GC column and into the Poropak Q column. The amine with its interacting groups traveled much slower. The flow arrangement at this point in the analysis is shown in Figure 2. After passing through the Poropak Q column the light components flowed to the detector. Upon elution of the light components, the switching valve was moved to position 2 as shown in Figure 3 and the amine eluted from the Tenax-GC column through the restrictor valve and to the detector. Thus, the bypass protected the Poropak Q column from irreversible adsorption or deactivation by the amine.
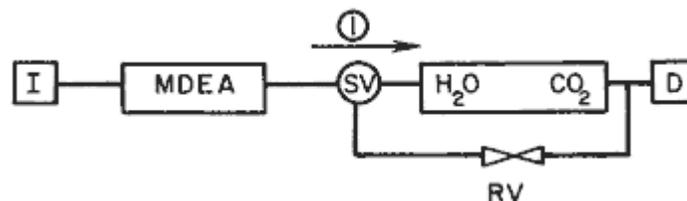

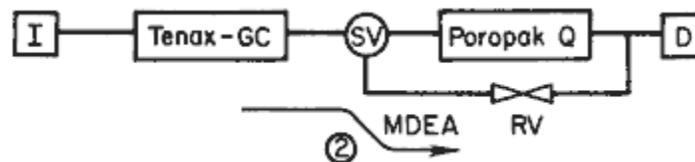Figure 2. Initial position of GC switching valve.

Figure 3. Final position of GC switching valve.

Operational Problems:

A number of trial injections were made and several operational problems developed. Since the helium carrier gas did not pass through a purifier, a baseline drift resulted. The problem was corrected by inserting two purifiers in the helium line. A large molecular sieve column removed water and a high capacity gas purifier manufactured by Supelco catalytically removed small amounts of oxygen and water.

Due to the high injection port temperatures necessary to vaporize the amine, the injection septa sealed poorly. The poor septum seal resulted in imaginary peaks (due to leaking of helium out of the septum during an injection) and poor reproducibility (some of the sample leaked out between the septum and syringe needle). To solve the problem, a new high temperature sandwich type septum was installed. A routine procedure of changing septa after about 20 injections proved satisfactory.

Occasionally the syringe needle was inserted too far into the GC and the actual sample injection point was past the vaporization block. The initial oven temperature was not high enough to instantly vaporize the sample. An initial column temperature of 120^oC was selected to prevent amine condensation. Regular regeneration of the columns and detector was important due to adsorption of MDEA.

Optimum GC Operating Conditions:

A variety of operating conditions were tested with the optimum combination giving good separation of all components in 8 minutes. The reproducibility of each analysis was +/-2%. The best operating conditions for the GC proved to be:

- Injector/detector temperature – 270^oC
- Initial column temperature – 120^oC
- Final column temperature – 240^oC
- Rate of temperature program – $20^oC/min$
- Detector current – 60 mA
- Carrier gas flowrate – 40 ml/minute
- GC attenuation – 1
- Integrator attenuation – 4

The switching valve was actuated at an oven temperature of 180^oC.

RESULTS AND VALIDATION OF GC TECHNIQUE

Sample chromatograms illustrating the separations for H_2S, CO_2, H_2O, MDEA and several light hydrocarbons are shown in Figures 4 through 7. In Figure 4, the sample contained CO_2 dissolved in a 10 wt. % MDEA solution in water. The GC operating conditions given in the previous section were used in this analysis. Excellent separation and sharp peaks were obtained. In Figure 5, a solution of H_2S, CO_2, MDEA and water was also analyzed using the GC operating conditions given in the previous section. Again, good separation and sharp peaks were obtained.
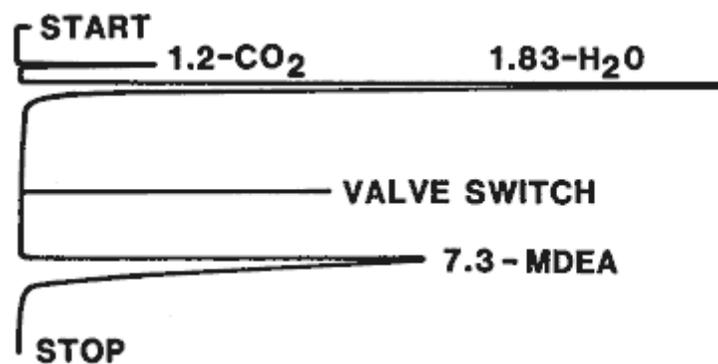

Figure 4. GC results using TENAX-GC and POROPAK Q columns with temperature programming.

START

2.38-CO$_2$

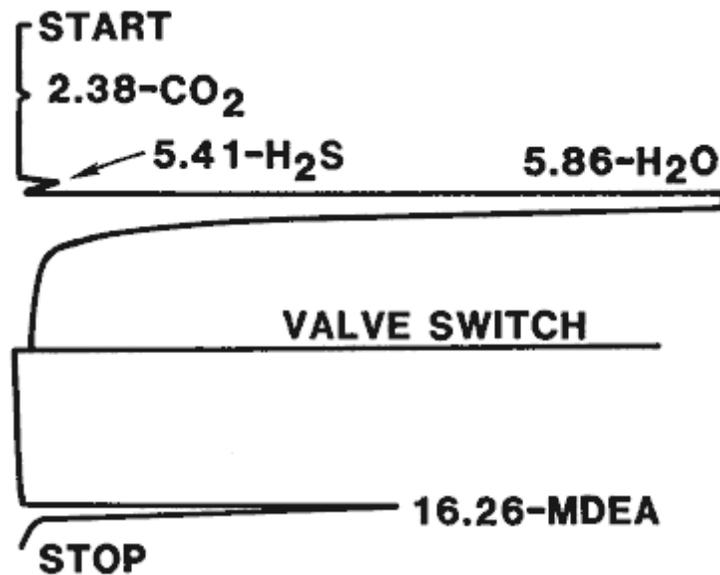5.41-H$_2$S   5.86-H$_2$O

VALVE SWITCH

16.26-MDEA

STOP

Figure 5. GC results using TENAX-GC and POROPAK Q columns with temperature programming.

At atmospheric pressure, insufficient quantities of light hydrocarbons could be dissolved in MDEA solution for detection using the current method. Several injections of calibration gases were made to demonstrate the separations possible. The GC output for a gas containing N_2, H_2S and C_3H_8 is shown in Figure 6. As noted in Figure 6, this analysis was performed at an isothermal column temperature of 80°C. The chromatogram for a gas containing N_2, O_2, CO, CH_4, CO_2, C_2H_4, C_2H_6, C_3H_6 and C_3H_8 is shown in Figure 7. The column temperature was again isothermal at 80°C. As can be seen from Figure 7, the N_2, O_2, CO_2 and CH_4 eluted at the same time. This separation needs to be improved. Good separation was obtained between C_2H_4 and C_2H_6 as well as between C_3H_6 and C_3H_8.

START   1.65-N$_2$

5.71-H$_2$S
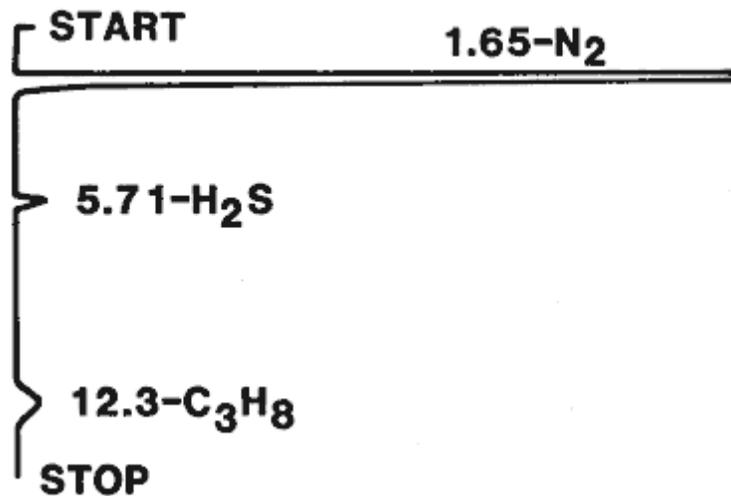
12.3-C$_3$H$_8$

STOP

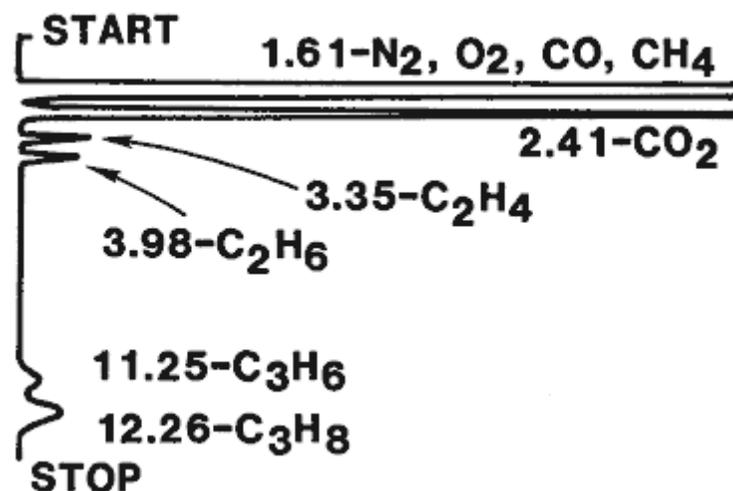Figure 6. GC results using TENAX-GC and POROPAK Q columns at 80°C.

Figure 7. GC results using TENAX-GC and POROPAK Q columns at 80°C.

At the present time, the new GC technique has been compared to the wet chemistry titration for CO_2 only. The titration methods outlined in the Dow Gas Conditioning Fact Book (1962) [5] were used for the comparison. Samples were prepared by bubbling CO_2 through aqueous MDEA solutions and analyzed by GC and titration.

The results are compared in Figure 8 where a 45° line represents perfect agreement between the two methods. As seen in Figure 8, the wet chemistry titration values were slightly greater than the GC result at high CO_2 concentrations. The deviations could be due to random errors in both techniques. Only a limited number of comparisons have been made at the present time. Some of the deviations could also be due to the difficulty in determining the exact titrimetric end points or both. The end point is not distinct and a few drops of acid or base are enough to explain the discrepancy. Another error could have resulted from exposure of the titrated solution to the atmosphere for brief periods.
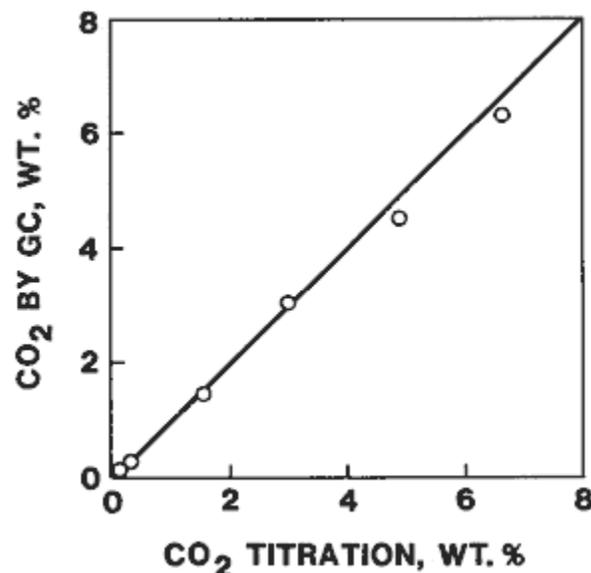

Figure 8. Comparison of analysis for CO_2 in MDEA by gas chromatography and titration.

The GC method has several advantages over the titration in that it is faster, less susceptible to operator error, specific to the compounds of interest and more reproducible. The GC method has another outstanding advantage since it can be equipped to perform online sampling at the process pressure and temperature. Accurate sampling of rich amine streams is difficult due to flashing and possible loss of both the acid gas and light hydrocarbons. At

pressures below about 100 psig, the light hydrocarbon content of amine solutions is low and does not present significant problems. However, in the range from about 100 psig to 1000 psig and higher, the light hydrocarbon losses can be quite important. Depending on the solution loading, acid gases can flash upon sampling at almost any pressure. Thus, using previous practices, samples must be taken in a sample bomb or a bag. The volume of the liquid and the flashed gases must be measured individually. The liquid is analyzed for the H_2S and CO_2 content by titration and the gases are analyzed by GC.

With the present GC technique, a sample loop may be added to the GC. This would allow the GC to be placed on-stream for sampling at the stream temperature and pressure. The pressure on the sample would be released after the sample loop is filled and upon injection of the loop contents into the GC. At this point, flashing is of no consequence since all of the sample will be vaporized in the injection block.

SUMMARY AND CONCLUSIONS

A gas chromatographic method has been developed to analyze amine solutions for acid gases, hydrocarbons, water and amine content. Good separations and sharp peaks were obtained for most components with Tenax-GC and Poropak Q columns when combined with temperature programming. The GC method has numerous advantages over the titration methods. These include approximate 10 minute analysis time, better reproducibility, the capability for on-line sampling and fewer interferences. The GC method agreed very closely with titration results for CO_2 analysis. Comparisons for the other components have not been completed at the present time.

ACKNOWLEDGEMENTS

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