

Acid Gas Loading Error Analysis: Is The Analysis Full of Error Or Is There Error in The Analysis?

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ABSTRACT

The industry Amine Best Practices Group (ABPG) reported several years ago on the errors that can be expected for amine strength determination by titration. A similar exercise is repeated here for acid gas loading analysis by standard pH and colorimetric titration methods. The errors are quantified with the errors in amine strength factored into the picture. Errors are classified into: 1) measurement errors, and 2) errors from oversimplified assumptions of the system chemistry. A set of expected uncertainties for standard H₂S and CO₂ loading measurements is furnished that can be weighed into the decision making process for establishing safe amine unit operations. A new method for determining CO₂ loading with typical analytical precision by using only pH titration with a strong acid (HCl) is also presented.

Introduction

Acid gas loading in alkanolamine solutions is one of the most important and commonly used parameters for monitoring the performance of gas treating units. Loading errors can have serious consequences. For example, if lean loadings are actually lower than measured, then excessive solvent circulation and energy consumption may be the result, unbeknownst to operations. If the real loadings are actually higher than measured, then either treating objectives may not be met at all or, far worse, corrosion will spiral into the unmanageable. Today's world energy needs demand greater reliability and better efficiency of hydrocarbon treating units. Increasing awareness of the corrosion and safety implications associated with elevated rich amine loading has led many operating companies to establish internal guidelines or standards that set hard limits to operations. While this addresses the safety and reliability issues, it should be recognized that one consequence is leaving some profit on the table. In cases where the treating capacity limits a hydrocarbon processing unit's ultimate throughput, the lost profit can be astronomical. Shaving even a few per cent from these lost profit figures can be hugely significant.

The questions then become, "How accurate does the acid gas loading measurement need to be?" and "How does this compare with how accurate the measurement actual is?". There are several vantage points from which one can view the importance of solvent loading:

- *The Operator* wants to know what is floating around in solution for safe and reliable operation (corrosion and environmental performance), to maximize the refinery or gas plant's throughput and receive a nice year-end bonus.
- *The Plant Engineer* is interested in performance monitoring, troubleshooting and optimization, and planning for future projects
- *The Design Engineer* needs to model the existing plant for robust project design, so uncertainty of analysis in some regards dictates the level of judiciousness needed for a design margin, and to ensure passing a performance test
- OGT: As vendors of the ProTreat™ rate-based mass transfer amine simulation software, we are sometimes asked why amine simulations, both ours and those of our competitors, do not always match plant measurements. To some extent, all models must be tuned to field data so measurement accuracy is paramount.

These vantage points are really all interconnected, with the effect of errors on one aspect or focus of treating impacting the other centers of attention as well.

In this paper we focus on the errors to be expected in amine sample analysis for amine strength and acid gas loading using pH titration via standard glassware and using an automatic titrator. Titration curves are related to detailed solution speciation as calculated by the ProTreat process simulator. Virtual pH titrations are carried out using Microsoft® Excel® to drive ProTreat simulations of the process equivalent of titration. The virtual titrations are validated against laboratory pH titration curves and the efficacy of using color indicators is discussed. Finally, the results of numerous virtual titrations are interpreted in terms of errors in measured acid gas loading for (a) a gas plant removing primarily CO₂ with MEA, and (b) a refinery operation using MDEA to remove H₂S.

1. Effect of Amine Analysis Errors

In an isolated set of circumstances, an error made in measuring the concentration of one species or another in an amine solvent may seem like a small thing. But such errors can have quite far-reaching consequences. Figure 1 shows diagrammatically the influence of solvent analysis errors on several facets of gas treating.

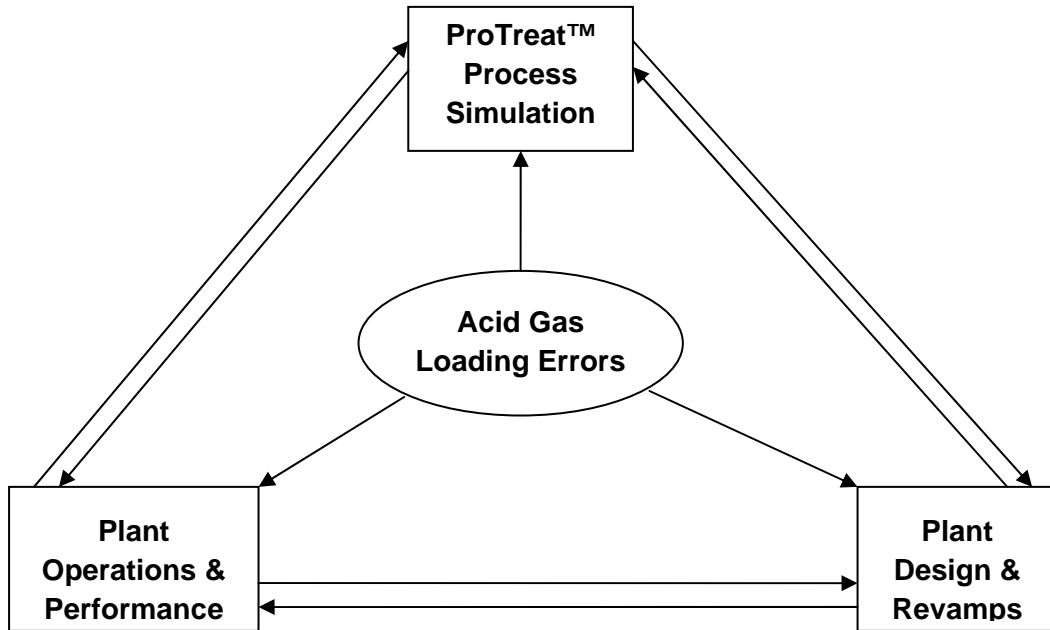


Figure 1 Solvent Analysis Errors—What They Affect

Analysis errors can affect decisions as to how a plant is operated, and on its measured *versus* actual performance. For example, if measured solvent H₂S lean loading is too low because the sample's integrity was not protected from oxidation of H₂S to other sulfur compounds, a completely erroneous picture of treating performance will result. Similarly distorted pictures will result when errors are made in the analysis of valid samples. Often, treating performance is assessed with the aid of simulation tools, and sometimes the simulation tools are adjusted to reflect measured performance. So analysis errors can lead not only to an incorrect picture of the plant's performance, but also to an improperly adjusted modeling tool.

Analysis errors can also affect revamp decisions and result in expensive and needless retrofits being undertaken. A correct solvent analysis might have pointed to something other than the solvent as the problem's cause, or it might have suggested a cleaner solvent to better utilize an already well-stripped solvent, rather than higher reboiler energy flow to reduce the lean loading below an already-adequate level. Again, many revamp and retrofit decisions are made using process simulation. Simulation tools commonly need to be tuned to data. If the data are wrong, the tool will be at least equally wrong, and so will be the decisions based on it.

The margins allowed in designing new plants and revamping existing ones are affected by sensitivity to uncertainties in such process parameters as the solvent purity, strength and loadings. Process simulation tools such as ProTreat are invariably used in design, and they are often used in plant operations and troubleshooting. Whatever uncertainties there are in the models used within the simulation tools, these uncertainties will (or should) be translated into design fat and sometimes excessive design safety margins are the result. There are always model parameters in any simulation tool that have to be adjusted and tuned over time to provide the best achievable performance *vis à vis* accurately reflecting field data. If tuning is done to erroneous data, the model will be at worst erroneous too, and at best a little skewed. In our

experience, one of the most common flaws in field performance data is incorrect solvent lean loadings. The other is the assumption that the solvent is clean.

As vendors of the unique, gas-treating process-simulation tool, ProTreat, we are often asked about model reliability on the one hand, and sometimes why model predictions differ from what's reportedly been measured, on the other. Almost invariably the answers come down to solvent analysis. More and more we find ourselves asking for a solvent vendor analysis and then scrutinizing it for at least the self-consistency that it all too often lacks. The best assumptions one can make about a lean amine solvent are that (a) it's contaminated, and (b) the reported lean loading (especially of H₂S) is probably wrong.

2. Conventions, Definitions and Prior Work in Amine Analysis

2.1. Amine Concentration

At previous Brimstone Sulfur Symposia, the industry Amine Best Practices Group (ABPG) has presented material on the analysis and associated errors that can be expected for amine strength determination (Amine Best Practices Group, 2004, 2005). The group found that much of the seeming error in amine strength determination can be attributed solely to the choice of definition of "amine strength". The following two of their preferred definitions are reproduced verbatim with key differences highlighted for clarity.

- "**Amine strength** is commonly understood as **the amount of amine** capable of reacting with acid gases, i. e. the working capacity of the solution. Amine strength is normally reported as weight % of the primary amine component in the total solution." This was referred to as the "**Original**" definition of amine strength.
- "**Titration** for amine strength is a measure of **the amount of base** in the solution that is **capable of reacting with acid gases** expressed as the **equivalent wt% of the amine primarily in use.**"

These definitions and their differences arise because titration is the most commonly used method for amine strength determination and, depending on the system, there can be multiple pH breaks from which different quantities can be inferred. Titration cannot distinguish between the different acids or bases in solution; it can only tell the "net" molar concentration expressed in units of the acid or base assumed to be in the solution.

These definitions are both measures of the amine capable of reacting with acid gas and are representative of the **operating** or **working capacity** of the amine solution. Free amine and Regenerable Free Base (RFB) are two other commonly used terms for this quantity. While useful in interpreting capacity in real operations, they tell nothing about the amount of total amine in solution, or in the case of the latter definition, about the amount of amine as distinct from the amount of base in solution. For operations personnel in a functioning plant, these definitions make perfect sense; however, from a scientific standpoint and from the point-of-view of fundamentals, they are much less appropriate. In our opinion, these definitions have arisen in part from the inherent limitations of the over-simplified amine analytical procedures that are commonly used in our industry. Most of these are based on using pH as a tracking indication value to an end point.

Working capacity of the amine can have multiple connotations and is subject to interpretation of end points if pH based titration is used for the amine strength measurement. This generates confusion. We avoid this topic altogether by using a total amine basis in this paper. The ABPG definitions related to operating or working capacity are referenced in this paper by the terms "operating" or "free" or "active" prefixing the words "amine strength". Since we are dealing with simulation, we need to know the "real" concentration of *all* the components

in the amine solution to obtain the most accurate rendering of the real process, we use the term “concentration” in lieu of “strength”, unless we are referencing a titrated quantity. This makes the subsequent treatment of error analysis much more straightforward because we can use calculations and the simulator to tell us what the “active amine” concentration (available to react with acid gases) is so that it can be related back to operating definitions. In this paper, the definitions related to the amount of amine in solution are:

- “Amine concentration” is the concentration of total amine in the solution, suffixed with the units being used.
- “Equivalent amine concentration as XX” is the amount of total amine in solution expressed as the concentration of amine species XX.
- “Amine strength” is the concentration of total base in solution expressed in concentration units of the amine type being referenced.

2.2. Acid Gas Loading

We use a strictly theoretical definition of loading. “Acid gas loading” is the number of moles of acid gas in solution divided by the number of moles of total amine in solution. This is numerically equivalent to the molar concentration of the acid gas divided by the molar concentration of all amine species in the solution.

3. Assessing Errors in Chemical Analysis

The random error in a specified chemical analysis is assessed from the errors inherent in the measurement of individual quantities using the methods of standard differential calculus. The difficult part is assigning values to probable errors in individual measurements. Consider a standard acid-base titration such as is done to determine amine concentration (normality) by titration with a standardized acid such as HCl. The normality of the amine is given by:

$$N_{Am} = N_{HCl} \times V_{HCl} / V_{Am} \quad (1)$$

There is an error associated with each of these terms. The aliquot of amine was probably pipetted from a larger sample of the solvent. Table 1 shows the errors associated with the fluid volume delivered from pipettes of various sizes. The volume of HCl needed to neutralize the amine content of the sample is usually determined by reading a burette (twice!). So even if the endpoint could be pinpointed with infinite accuracy there is still an error associated with volume of titrant delivered from the burette. Table 1 also shows errors associated with the volume delivered by burettes of various sizes.

Table 1 Tolerances in Delivered Volumes (from Kolthoff & Sandell, 1952)

Capacity (mL) Less Than And Including	Limit of Error (mL)	
	Transfer Pipette	Burette
2	0.006	
5	0.01	0.01
10	0.02	0.02
30	0.03	0.03
50	0.05	0.05
100	0.08	0.10
200	0.10	

Endpoints themselves can never be determined with perfect precision, not to mention accuracy. Color indicators used to determine endpoints undergo color change over a range of pH, with some indicators having a narrow range and others a very wide range. So it is important to select an indicator that has a distinct color change over a narrow range of pH values centered on the right pH. Amines are weak bases, HCl is a strong acid. Consequently, as shown by the virtual pH titration curve in Figure 2, the endpoint for the titration of MDEA against HCl, for example, occurs at a pH in the range from 2.7 to 5.0 with a mid-point value of about 4. Indicators that might be suitable for this titration are listed in Table 2. Setting aside any concerns

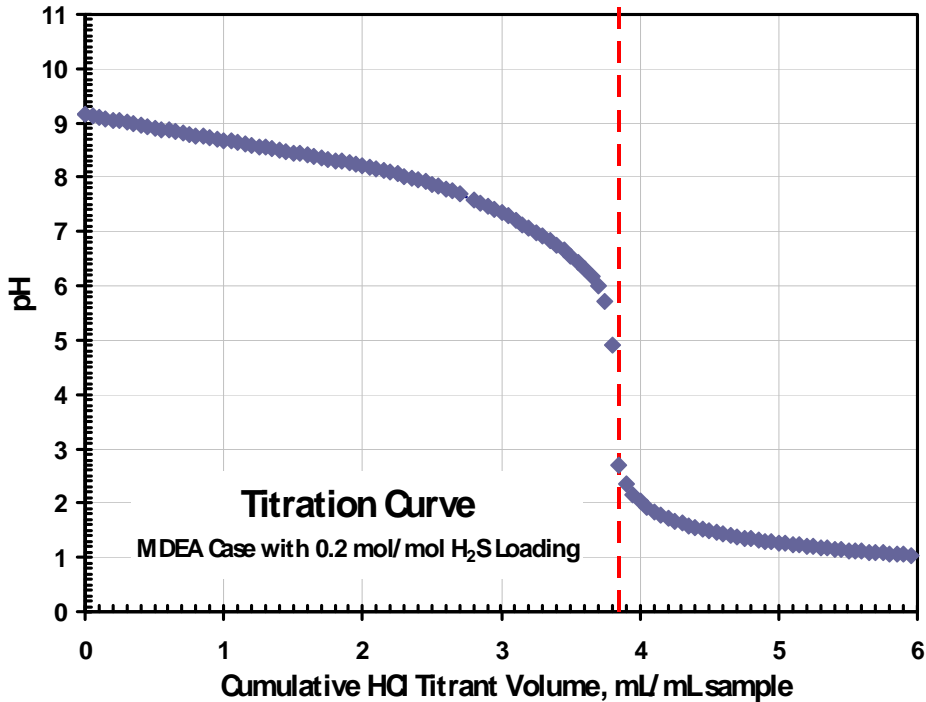


Figure 2 pH Titration Curve for HCl with MDEA

about color blindness on the part of the analyst (and this can sometimes be an over-riding consideration) the color change of methyl orange from yellow-orange to red is possibly not a sharp one compared with the purple to yellow change of bromphenol blue. Bromcresol green changes color perhaps slightly too far on the acid side of the neutral point and it's color change is over a rather wider pH range than the others; but its color change is distinctive. The point is

Table 2 Indicators Suitable for Titrating Amines with HCl

Trade Name	Acid / Base	Acidic Color	Basic Color	pH Interval
Methyl orange	Base	Red	Yellow-Orange	3.1 – 4.4
Bromphenol blue	Acid	Yellow	Purple	3.0 – 4.6
Bromcresol green	Acid	Yellow	Blue	3.8 – 5.4

that there is a certain degree of operator subjectivity with color indicators that does not exist with pH titrations, especially those using automatic titrators with software to pick out the endpoint

with almost uncanny precision. It must be pointed out, however, and as will be seen later in this paper, all endpoints are not as sharp as the one shown in Figure 2. Inability to pinpoint endpoints with precision can be the cause of the greatest uncertainty in loading measurements.

The absolute error in N_{Am} in Equation (1) is determined from the individual measurement errors by

$$\delta_{N_{Am}} = \left| \frac{\partial N_{Am}}{\partial N_{HCl}} \right| \delta_{N_{HCl}} + \left| \frac{\partial N_{Am}}{\partial V_{HCl}} \right| \delta_{V_{HCl}} + \left| \frac{\partial N_{Am}}{\partial V_{Am}} \right| \delta_{V_{Am}} \quad (2)$$

from which it can be seen how the errors accumulate. Errors in titrant standards (N_{HCl}) are usually small enough to be negligible. Pipetting errors in transferring the aliquot (V_{Am}) of sample to the titration flask are certainly manageable by selecting the right size equipment, but errors in the titer volume (V_{HCl}) depend on using the optimal equipment size (burette), method (indicator versus auto-titrator), technique, and whether the endpoint of a given titration can even be ascertained with reasonable certainty. This is the general approach we have taken to ascertaining errors in measured amine concentration and solvent loading.

4. Virtual Titration Using Process Simulation

4.1. Flowsheets

Titration is inherently a batch process in which a given volume of sample has added to it increasing amounts of a titrant. However, Titration can be modelled as a continuous process in which a stream of sample at a constant flowrate is mixed with a stream of titrant at a series of flowrates. Thus, the simple titration of an amine solution with HCl is represented as a set of steady-state simulations of the flowsheet shown in Figure 3, in which the titrant flow is varied from one simulation to the next. The amine sample is diluted with 10 times the flowrate of water

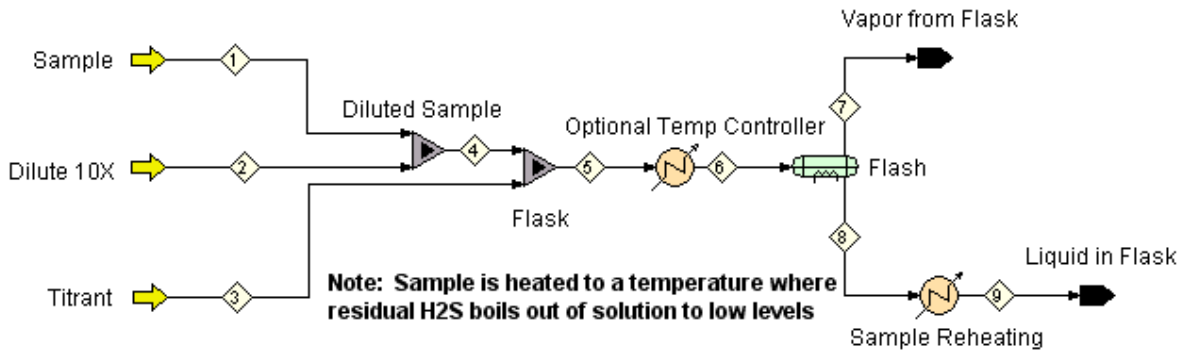


Figure 3 Flowsheet for Simple Titration With an Acid

before being mixed with HCl titrant of specified normality whose flowrate is such that the molar flow of HCl is some fraction of the suspected molar flow of amine. After dilution and reaction with HCl, the acid gases will have been driven out of solution. To complete this process the sample is heated and flashed. Then the liquid part of the sample is returned to the standard temperature of 25°C. The flash tank simply completes the task of removing released acid gases and the liquid from the flash tank is quite equivalent to the liquid mixture in a titration flask.

Figure 4 shows the flowsheet where NaOH is used for back-titration of a fully acidified sample (from which the acid gases have, therefore, been removed) of amine that may contain heat stable salts (HSSs) in addition to the excess acid used for acidification. Again flowrates of titrant and sample are in the same volumetric proportion they would have at some point in a titration. Replenishment water indicates the water makeup needed to replace the water driven off by heating and flashing shown in Figure 2. The critical factor in the process flowsheet representation of the titration is that the simulator is capable of fully speciating the solution at all times and at every stage of the titration. ProTreat is certainly capable of providing a detailed picture of the speciation of the mixture in any of the flowsheet streams, including the stream marked "Liquid in Flask".

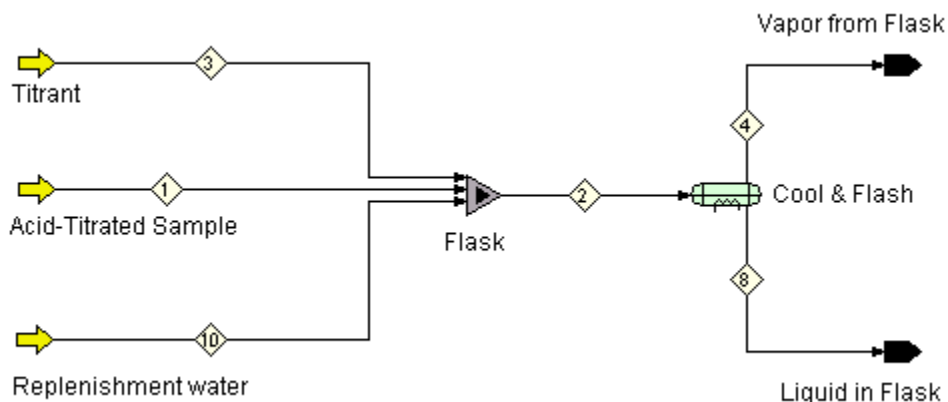
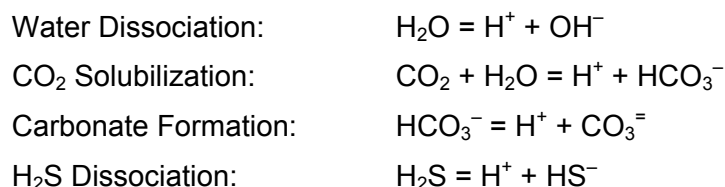


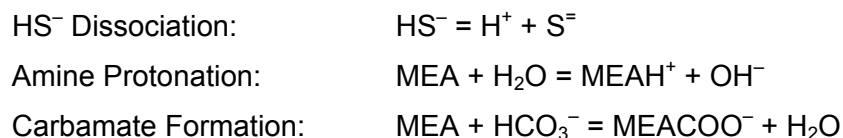
Figure 4 Flowsheet for Back Titration With NaOH

All that remains to do is to drive the simulator from a program such as Microsoft Excel using a macro written Visual Basic. This was the approach taken in the work being reported here. The sample flow was typically set at around 1.0 L/min for a 30 wt% MDEA or 50 wt% MDEA solution and 0.1 N titrant was added at flows between 0 and 6 L/min in 0.01 – 0.05 L/min increments. Thus, pH titration curves can be generated via process simulation and detailed speciation generated very rapidly (typically in less than a minute) with much reduced manual labor compared with a real analytical lab.

4.2. *Speciation*

In amine plant simulation, vapor-liquid equilibrium plays a key role, and central to phase equilibrium calculations is the detailed knowledge of the exact speciation of the solvent, i.e., of the exact distribution of all the ionic and molecular species in solution. The important molecular components in this endeavor are water, acid gases and amines, and generally each molecular species has two or three unique ions associated with it. For example, in a solution of MEA loaded with H₂S and CO₂ the following 12 species participate in determining vapor-liquid equilibrium: H₂O, H⁺, OH⁻, CO₂, HCO₃⁻, CO₃⁼, H₂S, HS⁻, S⁼, MEA, MEAH⁺ and MEACOO⁻. The concentration of each species, i.e., the speciation, is fixed by the following reaction equilibria:





For MDEA, carbamate is not formed, but all the other reactions occur with every amine. ProTreat's VLE calculations use the Deshmukh-Mather model. This model is based on the Debye-Hückel theory of electrolytes and it uses interaction parameters regressed to obtain the best possible agreement with literally well over 10,000 experimental VLE measurements for all the common amines plus a few of the less common ones. This is an activity coefficient model for the liquid phase and is combined with the Peng-Robinson equation of state for the vapor phase. For each of the seven reactions, there is an equilibrium reaction equation in terms of activities of the participating species. Other equations include atom balances on H, C, O and S, plus a charge balance giving 12 equations for the composition of the 12 species.

4.3. Validation

Either hydrogen ion, hydroxyl ion, or both, are involved in each and every reaction occurring when CO₂ and H₂S are present in the alkanolamines. Thus, it is to be expected that pH must be well represented by any VLE model that claims to accurately represent phase equilibrium data on a thermodynamically consistent basis. We recently undertook an extensive refitting of ProTreat's thermodynamic package to all available public-domain data and included proprietary data supplied by solvent vendors. In particular, great care was taken to ensure that the amine protonation reactions were as accurately represented as possible, and that solution heat capacities were accurately reproduced using temperature-dependent enthalpies calculated directly from the thermodynamic model itself. So how well does the pH virtual titration compare with laboratory results?

Figure 5 shows the laboratory-measured pH titration curve of a DEA sample highly contaminated with heat stable salts and compares it with a ProTreat-generated virtual titration curve. As long as the pH remains on the alkaline side of the pK_a value of the *least* acidic HSS, the simulation is within ± 0.1 or ± 0.2 pH units of the lab measured values. The agreement becomes quite poor, however, below a pH of about 5. Below a pH of about 5 the heat stable salts are no longer in the fully-dissociated state assumed in ProTreat. The simulator was designed to handle amine solvents as in alkaline solutions, where the HSSs are completely dissociated and the full concentration of all the HSS species enters into the charge balance equation alluded to in Section 5.2. It would be very easy to include temperature-dependent dissociation constant correlations for the HSSs in the charge balance equation of the thermodynamic model of the liquid phase. However, less than complete dissociation pertains only in acidic solutions where amine treating plants simply do not operate—it would be nice for generating titration curves involving HSSs but irrelevant to amine treating.

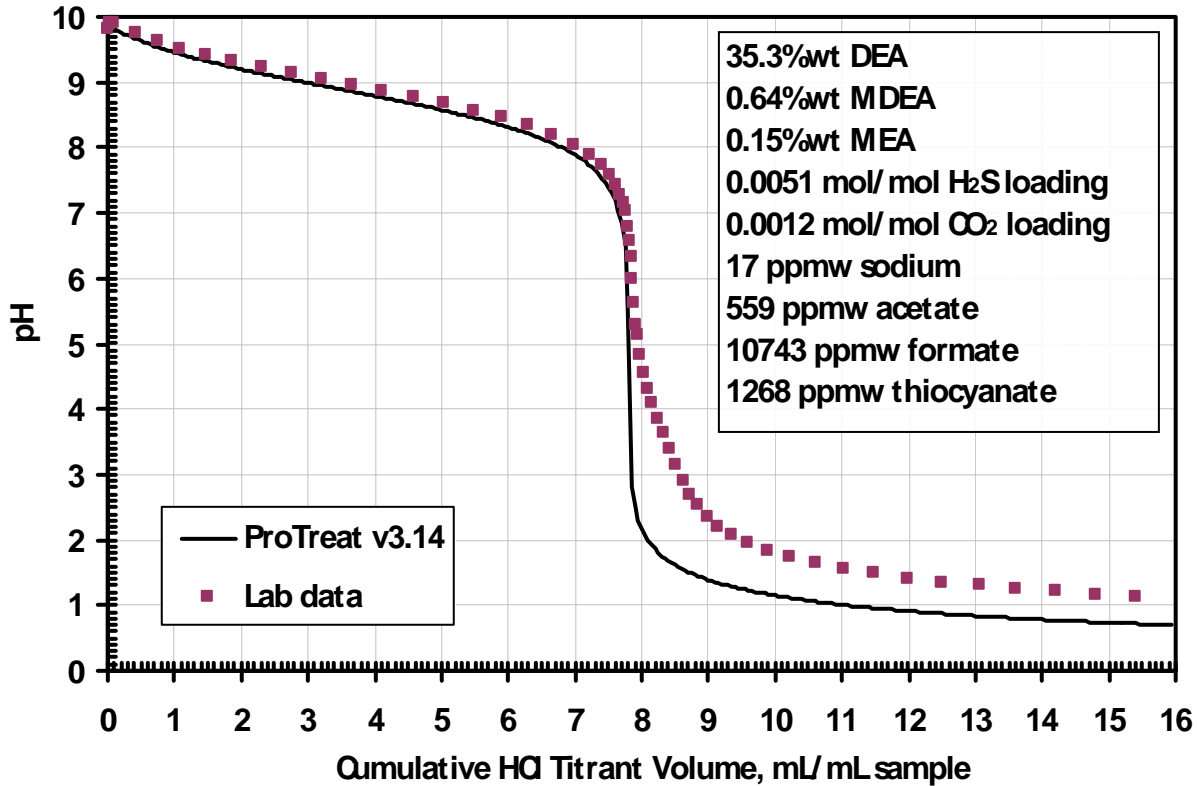


Figure 5 Measured and Simulated pH Titration Curves for DEA with HCl. Note the Very High Heat-Stable Salt Levels

6. Refinery Gas: H₂S-MDEA

During the most recent Amine Best Practices Group annual meeting, one member shared some analytical data on a refinery MDEA system treating mostly H₂S. The amine treating system in question was having some difficulties making specification, so it was decided to obtain a very thorough analytical shake-down of the lean amine. A gallon of amine sample was obtained and divided into individual samples for analysis by five different analytical labs of known repute. The statistics for the numerical values reported below are based on results obtained from the four labs that responded.

Although there is considerable scatter in the results from one solvent vendor lab to the next, the charge balanced lean loading for the average data, furnished in Table 3, is in very sound agreement with the range of measurements. A charge balance between the solution cations and anions *must* be obeyed for the solution to be electrically neutral. In this case, we took the most poorly defined ionic composition (the total lean loading) and adjusted the composition until the charge was in balance. A charge balanced loading that is drastically different from the data is suggestive of systematic error in the solution analysis data. Table 4 is a reproduction of a spreadsheet designed to ensure a charge balance on any amine sample by adjusting the least well-known quantity, the H₂S loading, to achieve this balance (Charge Balance Amine Analyses available at <http://www.ogtrt.com/demonstration.cfm>). Table 4 shows

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the charge balanced H₂S lean loading to be in agreement with measurements indicating that proper care was taken in sample preservation, handling, and analysis. In other words, the data appear to be trustworthy.

Table 3 Refinery MDEA Amine Analysis Raw Results

Parameter		Average	Range		Deviation %
MDEA (total)	%wt	43.4	42.8	44	2.0
DEA	%wt	0.6	0.6	0.6	0.0
HSAS as MDEA	%wt	2.2	2	2.6	19.3
Sodium	ppmw	129	110	147	20.3
Acetate	ppmw	514	251	844	81.6
Formate	ppmw	6834	5887	8440	26.4
Sulfate	ppmw	36	22	61	76.6
Thiocyanate	ppmw	1532	1129	2119	45.7
Total anions	ppmw	9288	7994	11453	26.3
H₂S loading	mol/mol	0.0012	0.0008	0.0017	53.0
CO ₂ loading	mol/mol	0.0002	0.0002	0.0002	0.0
Solution pH		9.9	9.7	10.1	2.9

Table 5 shows that ProTreat's predicted solution pH is within the range of the laboratory measured values. This substantiates our ability to perform virtual pH titrations using the ProTreat simulator. We thus concluded that this data would make an excellent starting point for the topic of error analysis.

Table 4 Charge Balance and pH Comparison for Refinery MDEA Case

For information on how to use this calculator, visit: http://www.ogtr.com/contactor.cfm and read Vol_2 Issue_2					
	Molecular or Ionic Weight	Species Analysis	Species Weight Fraction	Species Mole Fraction	Mole Fraction Charge
Amine	MDEA	wt%			
Free Amine	119.160	41.8	0.418352	0.10198	
Bound (AmineH+)	120.168	2.2	0.022450	0.00543	0.00543
Total		44.1	0.440802	0.10741	
Ions		ppmw			
Sodium (Na+)	22.990	129	0.000129	0.00016	0.00016
Potassium (K+)	39.098	0	0.000000	0.000000	0.000000
Formate (HCOO-)	45.017	6834	0.006834	0.00441	-0.00441
Acetate (CH3COO-)	59.044	514	0.000514	0.00025	-0.00025
Glycolate (C2H3O3-)	76.051	0	0.000000	0.000000	0.000000
Propionate (C2H5COO-)	74.078	0	0.000000	0.000000	0.000000
Oxalate (C2O4=)	88.019	0	0.000000	0.000000	0.000000
Phosphate (PO4-3)	98.004	0	0.000000	0.000000	0.000000
Chloride (Cl-)	35.453	0	0.000000	0.000000	0.000000
Sulfate (SO4=)	96.061	36	0.000036	0.00001	-0.00002
Sulfite (HSO4-)	80.079	0	0.000000	0.000000	0.000000
Thiosulfate (S2O3=)	112.127	0	0.000000	0.000000	0.000000
Thiocyanate (SCN-)	58.083	1532	0.001532	0.00077	-0.00077
Other Components					
Total acid gas as HS-	33.065		0.000158	0.00014	-0.00014
Water	18.015		0.549994	0.88685	
Total			1.000000	1.000000	0.000000
Total Moles per g solution	0.0344				
Calculated total acid gas loading	0.0013	mol/mol amine		Solve	
Calculation status	Converged				
Reported acid gas loadings	Average	Min	Max	Std Dev.	
H2S, mol/mol amine	0.0012	0.0008	0.0017	0.00064	53.0 %
CO2, mol/mol amine	0.0002	0.0002	0.0002		
Total, mol/mol amine	0.0014	0.0010	0.0019	0.00064	45.5 %

Table 5 pH Comparison for Refinery MDEA Case

ProTreat™ pre-dilution	10.112
ProTreat post 10x dilution	9.901
Avg Data	9.9
Data Low	9.7
Data High	10.1

6.1 Case Generation – Amine Strength

The first step in generating the cases examined in this paper was to titrate the lean amine sample with 1.0 N HCl for amine strength using ProTreat as given in the flowsheet of Figure 3 and the procedure described in Section 5.1. This generated a pH versus cumulative titrant curve like that shown in Figure 6.

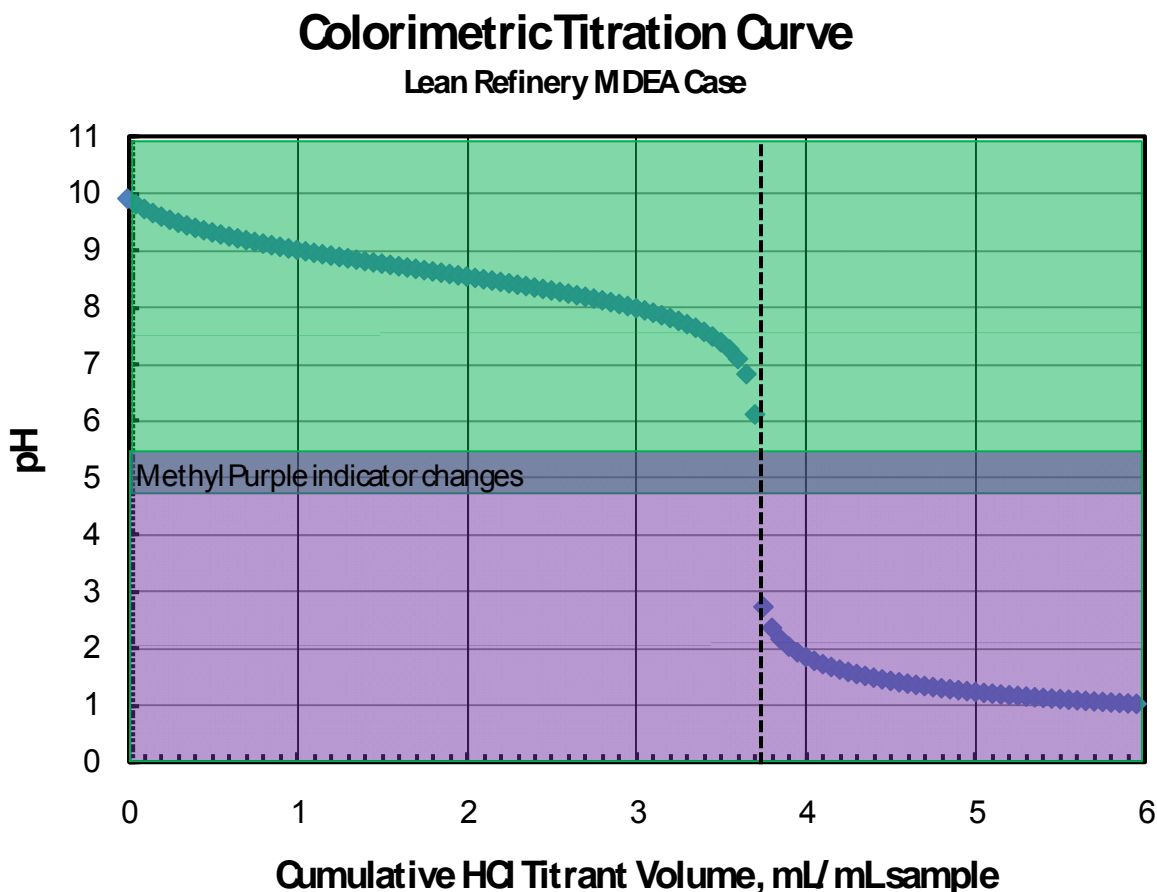


Figure 6 Lean Amine Acid Titration for Strength

From this plot, the amine strength can be related to the total moles of acid required to reach the end point as follows, assuming that one mole of acid reacts with one mole of amine:

Molarity of amine in original sample = gmol of acid / Liters of original amine solution

Wt% amine = Molarity of amine in original sample x Amine Mole Wt / (Solution Density) x Conversion Factor

Figure 6 shows that if methyl purple indicator were used, the end point would be 3.71 to 3.74 mL titrant per mL of amine sample. The range was obtained by zooming in on the end point in Excel and eyeballing the range of titrant where the indicator is changing. This titrant volume corresponds to 44.3%wt \pm 0.2%wt MDEA equivalent. Note that in titration, since the acid does not know that there is DEA or sodium also in solution, *we are forced to make the*

assumption that the amine is MDEA predominantly, and we'll use MDEA's molecular weight in the formula above.

We also evaluated the amine strength using methyl red, which is listed as an acceptable substitute—the amine strength found was 44.0%wt \pm 0.6%wt. Simple interpretation of the pH curve itself yielded the value 44.4%wt. The wide pH range for color change and lack of a distinct instantaneous color transition makes methyl red a somewhat poorer choice in this particular case, although the average strength is right in line with the data.

6.2 Case Generation – Rich Amine Loading

To generate the rich amine cases, the sample's H₂S loading was increased in 0.1 mole loading increments—these were the rich amine samples fed to ProTreat. The small residual amount of CO₂ loading was kept at a constant value equal to the lean loading. Cases were run both with and without the HSSs present to ascertain whether this factor would bias the results. Note that this required a separate amine strength run from the base case which included heat stable salts. For these rich amine cases, the heat exchanger block depicted in Figure 3 was manipulated to an outlet temperature of 220°F, sufficient to drive the acid gas from the sample at the acidified pH.

Each acidified rich amine case was replenished with water, cooled to 25°C, and then back titrated with NaOH in a separate simulation as shown in the flowsheet of Figure 4. A sample pH back titration curve is shown in Figure 7 for the 0.2 mol/mol rich H₂S loading case. As base is added to the acidified amine, excess acid and heat stable salts are first neutralized, culminating in the end point at about 1.7 mL/mL. Between this end point, and the final end point at 5.68 mL/mL, the amine is being deprotonated. This is revealed by the speciation.

Of particular interest in Figure 7 is the difference in titer volume between the final end point and the pH of the original rich amine sample (prior to acidification). Since nothing else should technically be reacting in this pH range, the amount of NaOH required should be proportional to the protonated amine in the original rich amine sample. By making this statement, again we *assume* one mole of base would have reacted with a mole of acid to begin with, and one mole of acid is equal to one mole of acid gas. This may not always be the case in a contaminated system, as will be discussed later.

In this manner, titration runs were repeated at different loadings to calculate the “experimental” H₂S loadings for comparison with the original loadings that were input into the case in question. Using the differential method of error analysis, we were able to generate a set of expected uncertainties for the experimental H₂S loadings in this Refinery MDEA Case.

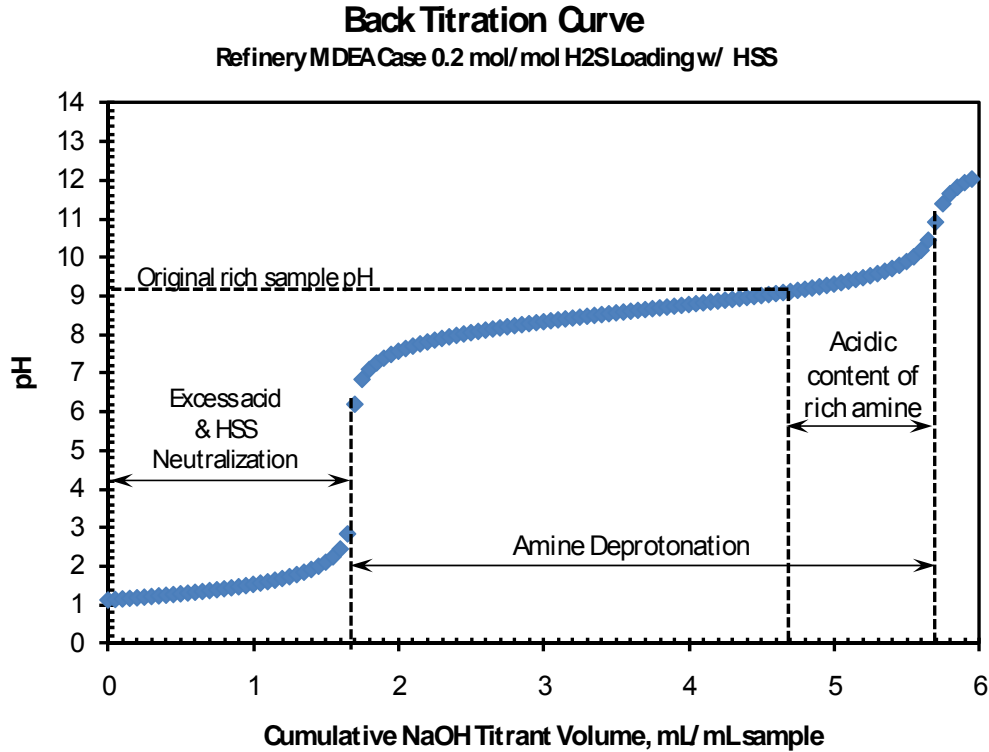


Figure 7 Back Titration Curve for Refinery MDEA Case

6.3 Case Results – Rich Amine Loading

Table 6 is a summary comparison between the H₂S loadings derived by virtual titration and the original input data that was used in ProTreat. The nominal errors in the measurement are seen to be comparable to the true errors in the measurements for those cases where heat stable salts (HSS) are not included.

In titration one assumes that one mole of titrant is equivalent to one mole of the component being titrated, and that *there is only a single species being titrated*. If the amine sample contains HSSs, the HSSs are also participants in the back titration, violating the single-species assumption. The HSSs cause over-measurement of the loading using this method. The extent of the over-measurement is proportional to the level of contamination and tends to wash out at the higher acid gas loadings.

A further observation is that the accuracy of the titrations in practice is limited by the Virtual Titration operator's ability to eyeball the inflection points in Excel charts. The low slope of the pH versus titrant flow in several instances made it difficult to ascertain precisely the titer volume around the rich amine pH at the inflection- or end-point (see Figure 7). This appears to be a fundamental limitation of the back titration method evaluated here. For the next case, we resorted to greater precision by reducing the flow interval step size and numerically calculating the first and second derivatives of pH with respect to flow, to help pin-point the inflection- or end-point.

Table 6 Comparison of Virtual Titration Loadings to Original ProTreat Input Refinery MDEA Case

Input H ₂ S loading, mol/mol	0.100	0.200	0.400	0.600	0.800
Loading per Virtual Titration	mol/mol				
System with H ₂ S and Na ⁺	0.132 ± 0.002	0.254 ± 0.004	0.452 ± 0.006	0.675 ± 0.009	0.88 ± 0.01
System without H ₂ S and Na ⁺	0.096 ± 0.002	0.203 ± 0.003	0.393 ± 0.005	0.596 ± 0.008	0.82 ± 0.01
% Error for Virtual Titrations	%	%	%	%	%
System with H ₂ S and Na ⁺	31.7	26.9	12.9	12.5	10.0
System without H ₂ S and Na ⁺	-4.2	1.4	-1.8	-0.7	2.5

7. Natural Gas: CO₂-MEA

7.1 Colorimetric Method

A member of the ABPG shared a common vendor field method which employs NaOH titrant with a thymolphthalein indicator to determine total acid gas loading. This particular indicator is clear at pH values below 8.8 and is blue for pH above 10.5. We decided to run some virtual titrations at differing CO₂ loadings in 20%wt MEA to check the validity and error associated with this procedure. Unfortunately (and surprisingly), the starting pH for most MEA-CO₂ systems appears to be in the range in which the indicator is either about to, or has just, changed color. Clearly, the indicator is useless for the purpose intended—it’s the wrong indicator. A sample titration curve for the 0.1 mol/mol CO₂ loading case is presented in Figure 8.

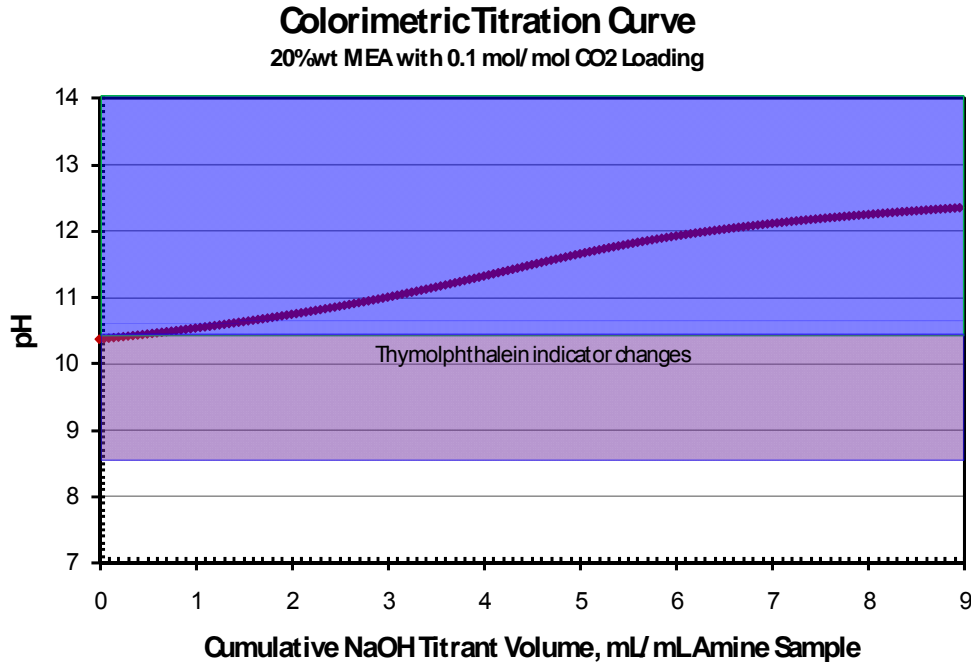


Figure 8 Sample Colorimetric NaOH Titration of MEA

Only at CO₂ loadings above 0.5 mol/mol does the pH of the amine stay below the value of 8.8 where the indicator begins changing. To complicate matters, we also noted that there is not a really clear inflection point in the pH curve in the indicator pH transition range.

Acid Gas Loading Error Analysis

Because of the large amount of error associated with simply judging where the indicator had changed color, a decision was made not to calculate explicitly the measurement errors for this method as they would clearly be dwarfed by the titration interpretation error. Instead, we chose to make an arbitrary assumption that the pH indicator would change in a 0.2 unit window between pH of 10.3 and 10.5 as the range of uncertainty. With the NaOH titer volume corresponding to these two pH readings, we then calculated the results by the vendor's formula.

$$\text{Loading} = \text{Moles Acid Gas} / \text{Moles Amine} = N \times A \times G / (M \times \text{Wt}\%)$$

where: N = Normality of NaOH

A = titer volume of NaOH, mL

G = Amine factor (6.0 for MEA), which is a function of the mole wt and specific gravity of the solution

The results of this method are compared with the original input CO₂ loading in Figure 9. The analytical method appears to under-predict the CO₂ loading below about 0.2 mol/mol actual loading. As the true loading increases, the predicted CO₂ loading becomes increasingly high compared to the true input data. Figure 9 can be used to get an idea of the error that can be expected from this method—it is certainly well above the experimental measurement errors of 4% or less for the H₂S loading back titration method in the Refinery MDEA case. This suggests a chemistry oversight or perhaps chemical interference, and will be further discussed later.

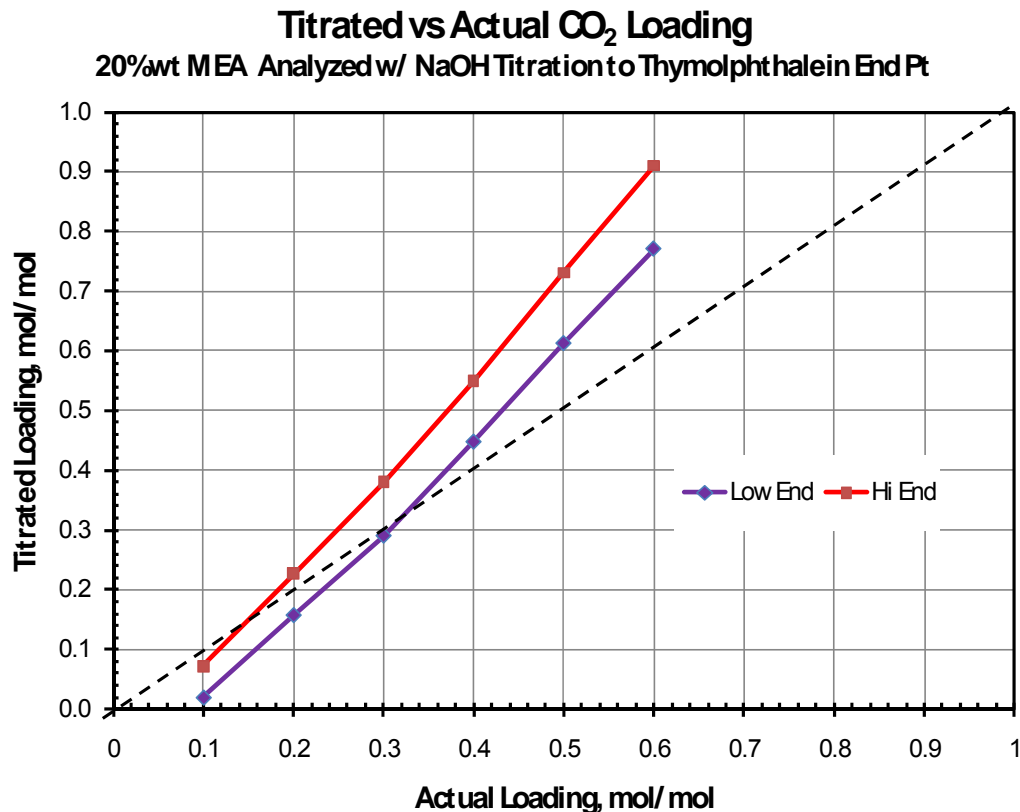


Figure 9 Errors and Uncertainty for CO Loadings by Thymolphthalein Color Titration Method

7.2 pH Back-titration Method

Noting the prior success that we had with the back-titration method for the Refinery MDEA-H₂S system, we decided to try this approach for the MEA-CO₂ system. Three loadings were evaluated: 0.1, 0.3, and 0.5 mol/mol for comparison with the thymolphthalein colorimetric method. Figure 10 shows a typical back-titration curve.

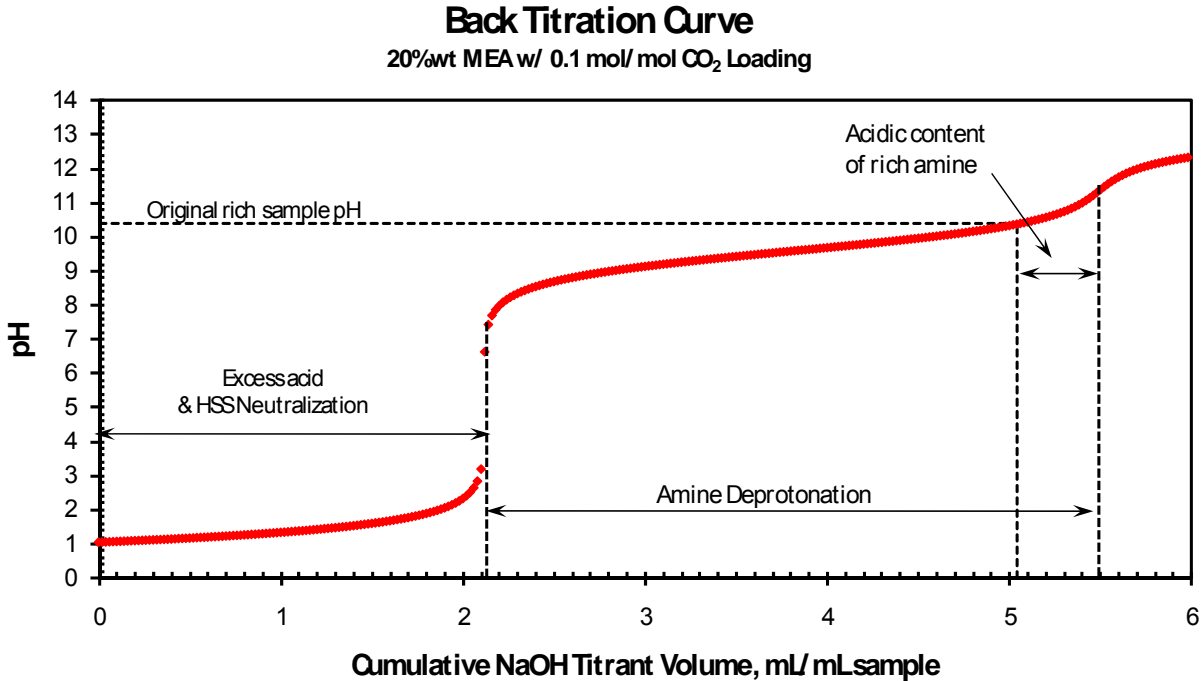


Figure 10 MEA Back-titration Curve

Although nice break points were observed for all three CO₂ loading cases examined with this method, the CO₂ loadings calculated were in very poor agreement with the original loadings input into the simulations. As noted in Table 6, this method appears to over-predict increasingly the CO₂ loading as the loading becomes higher.

Table 6 Results and Error Analysis for CO₂ Loading in MEA Back-titration Method

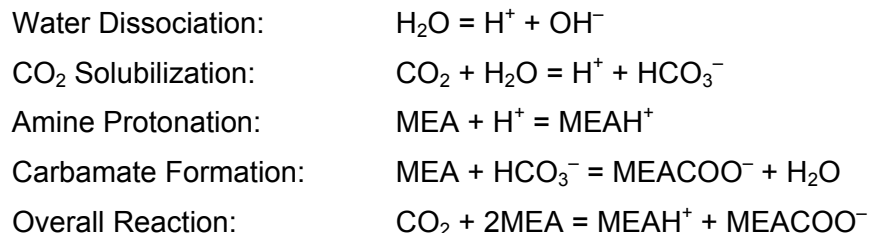
Input CO ₂ loading, mol/mol	0.100	0.300	0.500
Loading per Virtual Titration, mol/mol	0.131 ± 0.003	0.425 ± 0.006	0.79 ± 0.01
% Error for Virtual Titrations	31.0	41.7	58.0

Why is there such disparity? As with the MDEA-H₂S cases, one mole of acid is assumed to react with one mole of base, and a mole of acid is assumed to equate to a mole of acid gas. Since this all follows basic chemistry, speciation should provide a clue to the problem's cause.

Figures 11 and 12 show ProTreat's speciation results for the original *acid* titration of MEA loaded to 0.1 and 0.5 mol/mol CO₂ respectively. (It would be pointless to look at the back-titrations with NaOH for speciation because there is essentially no acid gas left in solution to speciate by the time the back titration is done.) Side-by-side comparison of these two cases

shows only one major difference—the 0.5 mol/mol CO₂ case has significantly higher relative carbamate concentration (about 15% of the total MEA compared with only 3% of the total MEA for the 0.1 mol/mol case).

Each mole of CO₂ that is in carbamate form is associated with two moles of MEA.



Since the amount of carbamate is changing with the loading, and the loading is unknown until the solution is analyzed, pH titration using caustic soda cannot be used to translate accurately back to the original acid gas concentration. Although it is beneficial from the standpoint of removing the interferences from HSS, the basic pH titration introduces interferences of its own. Carbonate also becomes increasingly active at the more alkaline pH values.

Figures 11 and 12 nevertheless suggest a possibly better way to assess the CO₂ content in MEA. There appear to be two discernable breakpoints in each acid titration curve. Referring to Figure 12 specifically, the dissolved CO₂ species first shift almost entirely to HCO₃⁻ by the occurrence of the first break point at 3.605 mL/mL and a pH of 7.63. The MEA is completely protonated at this pH. As the pH drops further from 7.63 to the second breakpoint at pH = 3.92 (7.201 mL/mL) the only reaction that appears to be of significance is the bicarbonate ion conversion to free, physically dissolved CO₂. *Having a single reaction with a single proton transfer makes pH titration a more meaningful indicator.* Furthermore, since nearly all of the CO₂ is reacting between these two end points, the amount of CO₂ in solution should be proportional to the difference in titrant volumes for these two end points, i.e., in this case, proportional to (7.201 mL/mL – 3.605 mL/mL). We saw in the amine strength titration that the total amount of amine in solution is proportional to the titer volume added to reach the last end point, i.e., amine in solution is proportional to 7.201 mL/mL. Therefore, the CO₂ loading can be expressed for this case as:

$$\text{CO}_2 \text{ loading} = (7.201 - 3.605 \text{ mL}) / (7.201 \text{ mL}) = 0.499 \text{ mol/mol}$$

This is almost exactly equal to the true loading!

This is an important finding—we just used a simple titration method and obtained nearly perfect results. *Knowing the detailed speciation pointed us to the right method* for this particular system. Note that to obtain these near-perfect results, it was critical that *only one reaction was occurring in the pH range being titrated*, and that one mole of acid gas corresponded to one mole of titrant. Also noteworthy is the method used to determine the break points of the pH curves in Figures 11 and 12. A tighter titrant injection interval was chosen to sharpen the resolution of our virtual titration curve so that numerical differentiation could be employed to pick the end points for us. In effect, we added mathematical software to the virtual titration to take human error out of the pH curve interpretation, similar to what is available in most auto-titrators.

Repeating the exercise for the 0.1 mol/mol CO₂ loading case of Figure 11 yielded an “experimental” loading of 0.099 mol/mol loading! The 0.3 mol/mol loading case was also run (but not plotted here) with a resulting experimental loading of 0.298 mol/mol!

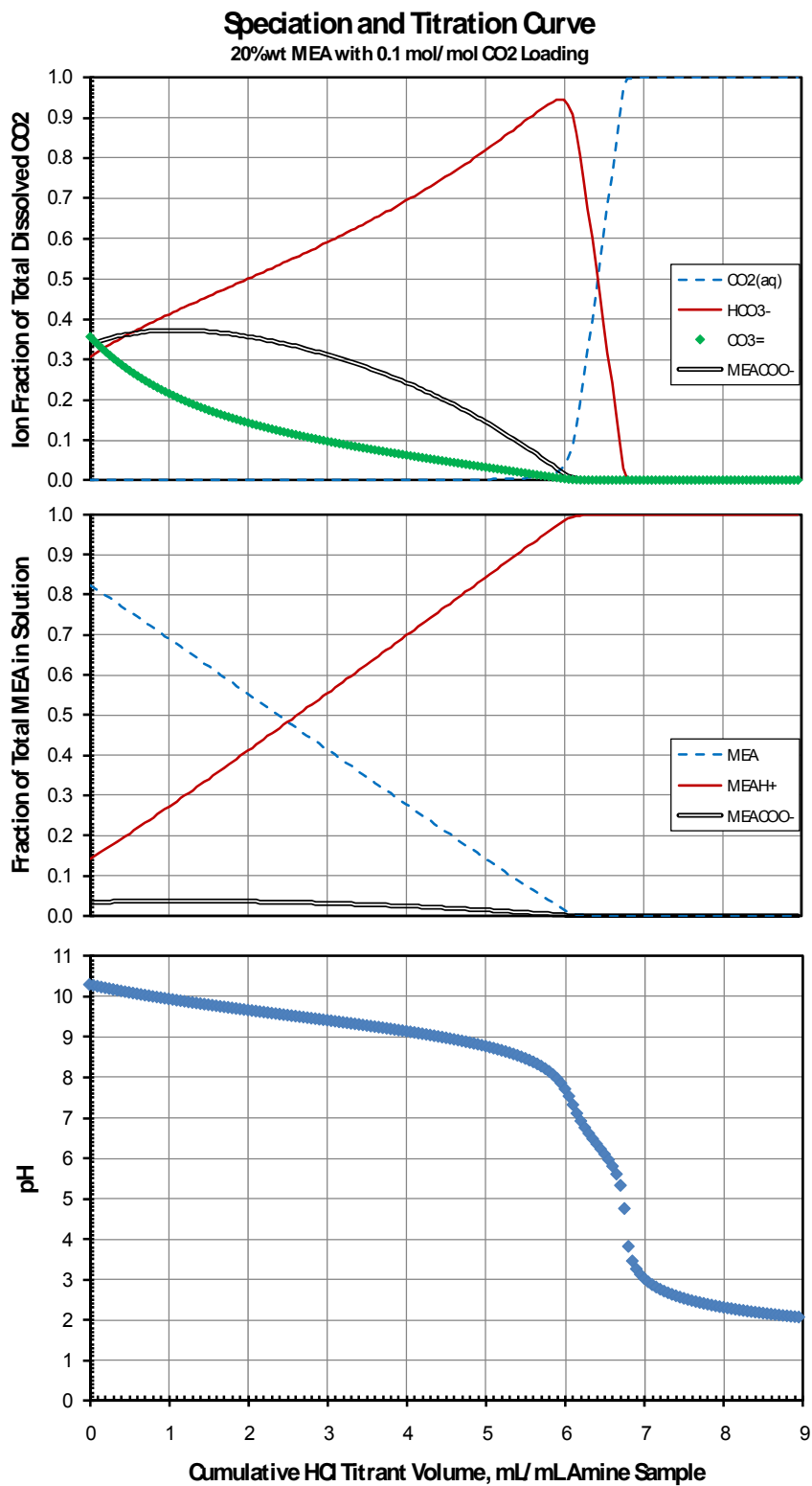


Figure 11 Speciation vs. pH for 0.1 mol/mol CO₂ Loading in 20%wt MEA

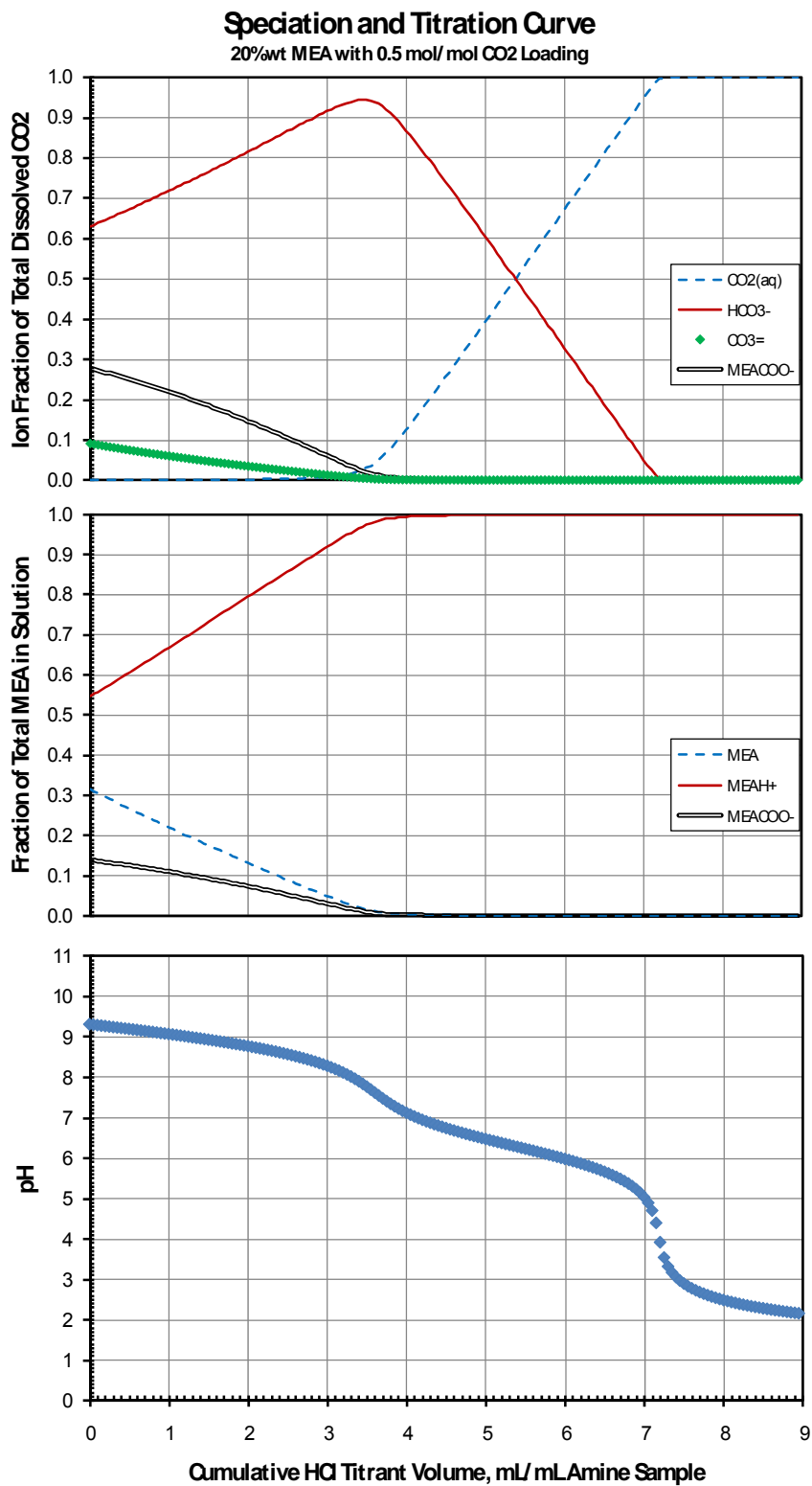


Figure 12 Speciation vs. pH for 0.5 mol/mol CO₂ Loading in 20%wt MEA

7.3 pH Acid Titration Method

We have made our way, in a roundabout manner, back to acid titration to quantify CO₂ loading in MEA by using the speciation data as a road map. The two break points that have been described also equate to the free and bound amine described back in the original ABPG amine strength determination work. From this knowledge, we can draw several analogies:

- HSSs will definitely interfere with this method as many common organic acids titrate in the pH range in question,
- For mixed acid gas systems, bisulfide ion will be titrating to H₂S over much of the same window that HCO₃⁻ is titrating to CO₂, and this will affect the results.

Similarly, for the error analysis, we are taking the difference of two titer volumes and dividing this by the total amount of amine in solution. The relative error in the measurements should be comparable to the Refinery MDEA case. The actual results obtained for this method are summarized in Table 7 below, and are consistent with this logic. Calculation sheets are shown in the Appendix.

Table 7 Results and Error Analysis for CO₂ Loading in MEA by Acid Titration Method

Input CO ₂ loading, mol/mol	0.100	0.300	0.500
Loading per Virtual Titration, mol/mol	0.099 ± 0.002	0.298 ± 0.005	0.499 ± 0.007
% Error for Virtual Titrations	-1.0	-0.7	-0.2

8. Summary

In all cases examined, errors in unforeseen or oversimplified chemistry far out shadowed the measurement errors nominally quantified for titration methods.

Straightforward titration using pH as an indicator for CO₂ loading needs to be avoided in general. In particular, interpretation of pH or color end-point in a CO₂-alkanolamine mixture under basic conditions is meaningless because carbonate and carbamate both titrate along with bicarbonate. Titration in and of itself assumes a fixed stoichiometry of acid with base but the speciation provided by ProTreat shows that this assumption is violated. Furthermore, ProTreat suggested that an acid titration on a clean solvent for CO₂ only, or with fairly low H₂S loading can probably be believed.

However, with the aid of detailed speciation, a method for using a simple acid titration that takes account of *two* break-points to determine CO₂ loading with high precision was proposed. The method was verified using virtual titration of three standard solutions and it was found that the CO₂ loading could be determined from pH titration to the precision normally expected from titrimetric methods.

The Achilles' heel of applying pH titration to alkanolamine solutions seems to be that the basic assumption of one mole of acid or base reacting with only ONE species is frequently violated. What exacerbates this problem is that neither the titration or nor titration technician knows what specific chemical component is actually being titrated. In our particular situation, we had a detailed chemical-thermodynamic model of the system so the virtual nature of simulation provided us with considerable insight. In general, however, when a detailed model of the solution chemistry is lacking, one must exercise great caution even in applying seemingly straightforward acid-base titrations.

9. Acknowledgments

We thank the industry Amine Best Practices Group participants who furnished the real analytical data that appears in this paper.

10. References

Amine Best Practices Group, *Evaluation of Amine Analytical Methods Part One: Amine Strength*, Proceedings of the Brimstone Sulfur Symposium, Vail, CO, Sept. 13-17, 2004.

Amine Best Practices Group, *Choices for Determining Amine Strength: Effects on Operations and Optimization*, Proceedings of the Brimstone Sulfur Symposium, Vail, CO, Sept. 2005.

Kolthoff, I. M., Sandell, E. B., *Textbook of Quantitative Inorganic Analysis*, 3rd Edition, MacMillan, New York, 1952

11. Appendix

Sample Error Analysis Worksheets

Acid Gas Loading Error Analysis							
Case:	MEA System w/ CO2 Only Loading Acid Titration						
Concentration of titration reagents (N)	0.1						
Original amine sample size used, mL	2						
Calculation Summary		Burette Measurement Error			Auto-Titrator Measurement Error		Actual Error vs. Sample, %
	Data	Calculated Value	Absolute Error, δ	Relative Error, %	Absolute Error, δ	Relative Error, %	
Total acid gas loading, mol/ mol amine	0.1	0.099	0.0022	2.19	0.0011	1.13	-1.2

Acid Gas Loading Error Analysis

Acid Gas Loading Error Analysis					
Total Differential Development Worksheet					
Case:	MEA System w/ CO2 Only Loading	Highlighted cells can be adjusted to study the effects of measurement inaccuracies on the final acid gas loading results.			
CO2 Loading	0.1 mol/mol amine				
Titer delivery method	Burette				
Loading Definition: moles acid gas / moles total amine = M_{ag}/M_{am}					
where:	M_{ag} = molarity of acid gas in original amine solution				
	M_{am} = molarity of amine in original amine solution				
1. Amine concentration (molarity units) = $M_{am} = M_{at}V_{at}/V_{am}$					
		Value	Absolute Error, δ	Relative Error %	Comments
where:	M_{at} = molarity of acid titrant	0.10	0.00003	0.03	Assumed for dilution of a known standard at standard 0.03% volumetric flask uncertainty
	V_{at} = volume of acid titrant used, mL	67.70	0.05	0.07	For a std 50 mL burette, drop size is 0.05 mL. This is about the maximum precision that can be obtained.
	V_{am} = volume of original, undiluted amine sample, mL	2.00	0.01	0.50	2 mL transfer pipette is ± 0.006 mL / 5 mL pipette is ± 0.01 mL
	M_{am} = molarity of amine in original amine sample	3.39	0.02	0.60	
Total differential:	$\delta M_{am} = dM_{am}/dM_{at} * \delta M_{at} + dM_{am}/dV_{at} * \delta V_{at} + dM_{am}/dV_{am} * \delta V_{am} =$				
where:	$ dM_{am}/dM_{at} = V_{at}/V_{am}$	33.9			
	$ dM_{am}/dV_{at} = M_{at}/V_{am}$	0.1			
	$ dM_{am}/dV_{am} = M_{at}V_{at}/V_{am}^2$	1.7			
2. Acid gas concentration (molarity units) = $M_{ag} = (V_{at} - V_{bt1})M_{bt}/V_{am}$					
		Value	Absolute Error, δ	Relative Error %	Comments
where:	V_{am} = volume of original, undiluted amine sample, mL	2.00	0.01	0.5	Volume and uncertainty are taken from above
	M_{at} = molarity of acid titrant	0.10	0.00003	0.03	Assumed for dilution of a known standard at standard 0.03% volumetric flask uncertainty
	V_{at} = reference volume of last endpoint, mL	67.70			This value is needed for only the volume scaling calculations. It does not show up in the total differential.
	$V_{at} - V_{bt1} = \Delta$ titrant volume (last endpoint - pH of original sample), mL	6.7	0.0707	1.06	For a std 50 mL burette, drop size is 0.05 mL. This is about the maximum precision that can be obtained. Taking the difference of two numbers the absolute error, $\sigma = (\sigma_A^2 + \sigma_B^2)^{0.5}$
	M_{ag} = molarity of acid gas in original undiluted amine sample	0.33	0.005	1.6	
Total differential:	$\delta M_{ag} = dM_{ag}/d(V_{bt2}-V_{bt1}) * \delta(V_{bt2}-V_{bt1}) + dM_{ag}/dM_{bt} * \delta M_{bt} + dM_{ag}/dV_{am} * \delta V_{am} =$				
where:	$ dM_{ag}/d(V_{bt2}-V_{bt1}) = M_{bt}/V_{am}$	0.05			
	$ dM_{ag}/dM_{bt} = (V_{bt2} - V_{bt1})/V_{am}$	3.35			
	$ dM_{ag}/dV_{am} = (V_{bt2} - V_{bt1})M_{bt}/V_{am}^2$	0.17			
		Value	Absolute Error, δ	Relative Error %	
3. Experimental total acid gas Loading = M_{ag}/M_{am} , mol/mol					
		0.10	0.0022	2.2	The relative error is the nominal measurement expectation due to random error. Any systematic error will be above and beyond this figure.
Total differential:	$\delta \text{Loading} = d\text{Loading}/dM_{ag} * \delta M_{ag} + d\text{Loading}/dM_{am} * \delta M_{am} =$				
	$ d\text{Loading}/dM_{ag} = 1/M_{am}$	0.295			
	$ d\text{Loading}/dM_{am} = M_{ag}/M_{am}^2$	0.029			
4. Actual error versus measured value of total acid gas loading =					
		-0.001 mol/mol			
		-1.2 % difference			

Acid Gas Loading Error Analysis

Acid Gas Loading Error Analysis																																			
Total Differential Development Worksheet																																			
Case:		MEA System w/ CO2 Only Loading																																	
CO2 Loading		0.1 mol/mol amine																																	
Titer delivery method		Autotitrator																																	
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V_{at} = reference volume of last end point, mL	67.70			This value is needed for only the volume scaling calculations. It does not show up in the total differential.																															
$V_{at} - V_{bt1} = \Delta$ titrant volume (last endpoint - pH of original sample), mL	6.7	0.0028	0.04	For an auto-titrator, piston steps are roughly $\approx 1/5000$ of the reservoir size. 20 mL would be 4-5 microliters. Taking the difference of two numbers the absolute error, $\sigma = (\sigma_A^2 + \sigma_B^2)^{0.5}$																															
M_{ag} = molarity of acid gas in original undiluted amine sample	0.33	0.002	0.6																																
Total differential: $\delta M_{ag} = dM_{ag}/d(V_{bt2}-V_{bt1}) * \delta(V_{bt2}-V_{bt1}) + dM_{ag}/dM_{bt} * \delta M_{bt} + dM_{ag}/dV_{am} * \delta V_{am}$																																			
where:		$ dM_{ag}/d(V_{bt2}-V_{bt1}) = M_{bt}/V_{am}$ 0.05																																	
		$ dM_{ag}/dM_{bt} = (V_{bt2} - V_{bt1})/V_{am}$ 3.35																																	
		$ dM_{ag}/dV_{am} = (V_{bt2} - V_{bt1})M_{bt}/V_{am}^2$ 0.17																																	
3. Experimental total acid gas Loading = M_{ag}/M_{am} , mol/mol																																			
<table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th></th> <th>Value</th> <th>Absolute Error, δ</th> <th>Relative Error %</th> <th>Comments</th> </tr> </thead> <tbody> <tr> <td></td> <td style="background-color: yellow;">0.10</td> <td>0.0011</td> <td>1.1</td> <td>The relative error is the nominal measurement expectation due to random error. Any systematic error will be above and beyond this figure.</td> </tr> </tbody> </table>							Value	Absolute Error, δ	Relative Error %	Comments		0.10	0.0011	1.1	The relative error is the nominal measurement expectation due to random error. Any systematic error will be above and beyond this figure.																				
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		$ d\text{Loading}/dM_{ag} = 1/M_{am}$ 0.295																																	
		$ d\text{Loading}/dM_{am} = M_{ag}/M_{am}^2$ 0.029																																	
4. Actual error versus measured value of total acid gas loading =																																			
		-0.001 mol/mol																																	
		-1.2 % difference																																	