

Better Alkanolamine System Operations Through Chemical Analysis

The Sulfur Recovery Symposium
Vail, Colorado, September 2010

By
Arthur L. Cummings (Presenter)
and Glen D. Smith
MPR Services Inc., Dickinson Texas
© MPR Services, Inc. 2010

ABSTRACT

Chemical analysis opens the door to understanding, responding to, and prevention of alkanolamine (amine) system operational difficulties. Unfortunately, the link between the analysis report and the amine system operation is often very foggy. The perplexity results from several factors that lead to misunderstandings, misinterpretations, frustrations, and mistrust of the lab. This paper attempts to dispel the fog by providing clear definitions of analytical terms, linking them to their operational importance, translating terminology from different sources to uniform set of terms, and exposing analytical methods that can mislead you. This presentation also provides questions you can ask your chemist to avoid operational pitfalls and get the intelligence you need from the analysis reports.

INTRODUCTION

An alkanolamine acid gas scrubbing system is an elegantly simple concept: a solution of water and alkanolamine absorbs acid gases from petroleum gas or liquid, and is pumped to a heated regenerator that releases the acid gases, and then the amine is cooled as it returns to the absorber. The amine solution circulates happily forever, the simple acid-base chemistry of the process can be monitored by a few analytical titrations (Table 1) and operators need be concerned with monitoring only temperatures, pressures, and flow rates and balancing the amine absorbing capacity with the acid gas demand of the incoming petroleum gas or liquid so that the product gas or liquid meets specifications. (The acid gas content of the sweetened product is, of course, the ultimate control measure, but is beyond the scope of this paper.) Such is the design of amine systems and the conditions for which the most common analytical methods were developed.

Table 1 Fundamental Analytical Parameters of Amine Solutions		
Parameter	Analyte	Description
Amine Strength	Free Amine (FA)	Amine available for acid gas absorption
Acid Gas Loading (AGL)	Rich Loading (RL)	Acid gas (H ₂ S & CO ₂) in the solution exiting the Absorber
	Lean Loading (LL)	Acid gas (H ₂ S & CO ₂) in the solution exiting the Regenerator
Water	Water	The remainder of the solution (if no contaminants)

If no contaminants accumulated in the amine system, this could be the extent of the analytical information required to operate. Unfortunately, contaminants do accumulate in amine systems and affect the equipment longevity and the success of the operation of the amine system. More unfortunate is the fact that the contaminants can affect the results of the fundamental analytical methods, misleading the operator, yet the operator continues to rely on these few simple tests for day-to-day operations.

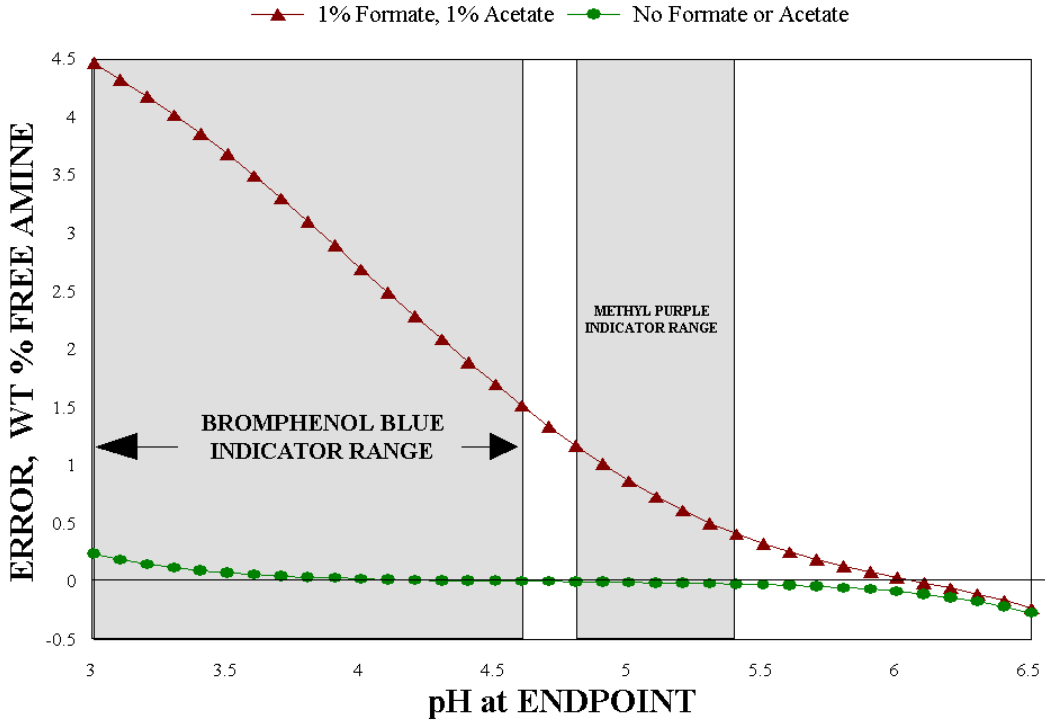
Increasing awareness of the effects of contaminants on operations has been accompanied by increasing understanding of the variety of contaminants that exist in amine systems. Common analytical methods have been adapted for, adjusted for, or misapplied to contaminants. Contaminant-specific analytical methods have multiplied. The amine system operator can now be confronted with a maze of analytical parameters, a blur of analytical results, and a host of analyte names and acronyms which can be ambiguous, confusing and even misleading.

BETTER ANALYTICAL METHODS ARE NEEDED

A prime example of misleading results is illustrated in Figure 1 and Table 2. When weak acids (such as formic acid, acetic acid, etc.) have accumulated in the amine solution, forming Heat Stable Salts (HSS), the titration to determine free amine can also respond to the weak acid anions. The choice of pH for the endpoint of the titration determines whether the free amine titration is accurate or over-estimates the amine strength. A pH or color indicator that provides accurate amine strength in a clean amine solution can grossly over-estimate the amine strength of a solution which contains weak acid anions (HSS or LL). Note, for example, in Figure 1, that Methyl Purple and Bromthymol Blue are both acceptable indicators for titration of clean amine solutions, but fail miserably if the solution contains significant weak acid HSS. The same is true for a pH “dead-stop” titration. The most common amine strength titration methods were developed for amine solutions with no contaminants. Thus, contaminants may cause errors.

Figure 1

**ENDPOINT pH AFFECTS ACCURACY
OF FREE AMINE TITRATION**



**TABLE 2
ERROR OF FIXED pH ENDPOINT TITRATION
45 wt% MDEA**

ACETATE wt%	FORMATE wt%	SODIUM wt%	ACTUAL FREE AMINE wt%	FOUND FREE AMINE, wt% at Endpoint pH		
				4.5	3.5	3.2
0	0	0	45.0	45.0	45.1	45.2
1	1	0	40.3	42.0	44.0	44.5
1	0	0	43.0	44.3	45.0	45.1
1	1	.5	42.9	44.6	46.6	47.1
1	0	.5	45.0	46.9	47.6	47.7

ENGINEERS AND CHEMISTS NEED AN UNDERSTANDING OF ANALYSES

Armed with the preceding information, the engineer responsible for the amine system can now ask the analytical chemist, “What endpoint indicator do you use for the amine strength titration?” If the chemist responds “bromphenol blue” or “pH 4.5” the engineer knows that amine strength results are probably higher than true, unless there are no weak acids in the amine solution.

The better titration methods require tracking pH or conductivity during the titration and determining the endpoints by inflexion points in the first or second derivative, respectively. Both pH and conductivity can provide accurate free amine results, but conductivity is preferred because it also provides clear endpoints for the weak acids (See Appendix A).

This and other difficulties with amine strength determination, and their effects on operations, are discussed at length in Amine Best Practices Group presentations at the 2004 and 2005 Brimstone Sulfur Symposia.

Before we seek to understand analytical methods, let’s clarify our understanding of the amine solvent itself.

THE AMINE SYSTEM IS SUPPOSED TO MAKE SALTS

The chemistry of alkanolamine solutions is quite simple, but is often described in terms which lead to a cloudy or incorrect view of amine interactions with acid gases and contaminants. Consequently, the understanding of analytical results because more difficult.

Alkanolamines are bases. Bases react with acids to make *salts*. Acid gases are absorbed and held in amine solutions because the amine makes a salt of the acid gas: The amine makes an anion from the acid gas so it cannot be a gas. As long as it is an anion, it cannot leave the amine solution.

The regenerable salts in Table 3 and the heat stable salts in Table 4 are written to emphasize the separateness of the ions. A *cation* is a positively charged molecule that is physically *dis*connected from its neighboring *anion*, which is an independent molecule with a negative charge. Anions and cations must be in equal numbers and uniformly distributed throughout the solution, but are continually changing partners. This view of ions is critical to the understanding of amine acid gas absorption and regeneration.

For example, H₂S absorbed in an amine solution is not bound to the amine. Rather, the amine has taken a hydrogen ion (H⁺) from the H₂S, creating an HS⁻ anion which cannot escape from the solution. The amine is bound to the H⁺, and does not readily release it. The only way for the HS⁻ to escape the solution is to take an H⁺ from an AmH⁺, thereby

recreating H₂S, which has low solubility and high volatility and will exit the solution, unless another amine molecule encounters it and takes one of its H⁺ away.

Acid gases are readily released from the thin films of liquid amine solution in an amine system regenerator, not because temperature “breaks the salts”, but because at higher temperatures AmH⁺ more readily releases its H⁺, and the anions of the acid gases readily take the H⁺ creating the gases that are less soluble and more volatile at elevated temperature.

Heat stable salts, such as those in Table 4, do not leave the amine solution in the amine system regenerator. The acids of these salts are generally stronger acids than the acid gases (thus not as readily keep the H⁺ offered by the AmH⁺), and are more soluble and less volatile than the acid gases (thus not as readily leave the solution). The HSS anions can be classed as weak acid anions (WAA) and strong acid anions (SAA). The functional distinction between WAA and SAA is seen in titration with acid in water: $WAA^- + H^+ \rightarrow HWAA$; $SAA^- + H^+ \rightarrow SAA^- + H^+$. In words: WAA consume H⁺ (making an acid molecule), SAA do not.

The last four entries in Table 4 exemplify non-amine heat stable salts: salts whose cation is a Strong Cation such as sodium or potassium. These are often called Inorganic Heat Stable Salts (IHSS) and are formed in amine solutions from addition of caustics (sodium or potassium hydroxide or carbonate). The last two entries illustrate that excessive concentration of Strong Cations makes heat stable salts of the anions of acid gases, causing the lean loading of the regenerated amine to rise. Strong Cation must never be allowed to rise to the level that any acid gas becomes heat stable.

Acid gas regeneration is aided by a low concentration of Amine heat stable salts, because they increase the population of AmH⁺ from which the anions of acid gases can take an H⁺.

Acid gas regeneration can be hampered by Strong Cations, because they have no H⁺ to give. Anions of acid gases are attracted to the strong cations because of their positive charge, and then must remain in the amine solution, because they cannot obtain an H⁺ from the strong cation.

Heat Stable Salts reduce amine strength, increase corrosivity, increase viscosity, increase density and displace water from the amine solution. All these have deleterious effects on amine system operations. It is thus very important to know what and how much of these salts are accumulating in one's amine system.

Table 3			
Regenerable Salts from Acids Gases in Amine Solutions			
Acid + Base → Cation + Anion			
<u>Acid</u>	<u>Base</u>	<u>Salt</u>	<u>Salt Name</u>
H ₂ S	Free Amine (“Am”)	AmH ⁺ + HS ⁻	Aminium bisulfide
CO ₂ + H ₂ O → H ₂ CO ₃	Am	AmH ⁺ + HCO ₃ ⁻	Aminium bicarbonate
HCO ₃ ⁻	Am	2AmH ⁺ + CO ₃ ⁼	Aminium carbonate
CO ₂	Am + Am	AmH ⁺ + AmCO ₂ ⁻	Aminium amine carbamate

Table 4			
Heat Stable Salts from Acids in Amine Solutions			
Acid + Base → Cation + Anion			
<u>Acid</u>	<u>Base</u>	<u>Salt</u>	<u>Salt Name</u>
Formic	Am	AmH ⁺ + formate ⁻	Aminium formate
Acetic	Am	AmH ⁺ + acetate ⁻	Aminium acetate
Propionic	Am	AmH ⁺ + propionate ⁻	Aminium propionate
Thiocyanic	Am	AmH ⁺ + SCN ⁻	Aminium thiocyanate
Thiosulfuric	Am + Am	AmH ⁺ + S ₂ O ₃ ⁼ + AmH ⁺	Aminium thiosulfate
Hydrochloric (HCl)	Am	AmH ⁺ + Cl ⁻	Aminium chloride
Sulfuric	Am + Am	AmH ⁺ + SO ₄ ⁼ + AmH ⁺	Aminium sulfate
Formic	NaOH	Na ⁺ + formate ⁻	Sodium formate
Acetate	NaOH	Na ⁺ + acetate ⁻	Sodium acetate
Acid gases are heat stable with caustics, for example:			
H ₂ S	NaOH	Na ⁺ + HS ⁻ + H ₂ O	Sodium bisulfide
HCO ₃ ⁻	KOH	K ⁺ + CO ₃ ⁼ + H ₂ O	Potassium carbonate

WHAT ANALYSES ARE NEEDED?

The first tier parameters affecting amine system performance are free amine and water content. The free amine represents the carrying capacity of the solution and the water content affects the acid gas absorption and desorption rates. The amine solvent supplier, amine system designer or the amine technical support person typically provides operators with recommended ranges of free amine and water for the particular application. Were there no contaminants in the amine system, the Table 1 analyses would be sufficient –

water could even be determined by difference. Contaminants are common in amine systems. Thus, in Table 5 are shown several parameters requiring analysis.

Table 5 Solvent Parameters of Amine Solutions		
<u>Parameter</u>	<u>Analyte</u>	<u>Description and role</u>
Amine Strength	Free Amine (FA); Regenerable Free Base (RFB)	Amine available for acid gas absorption
Reacted Amine	Bound Amine (BA)	Amine that has reacted with an acid and now carries an hydrogen ion: AmH ⁺ .
Total Amine	Total Amine (TA) = FA + BA; Actual Total Base (ATB)	All the amine in the solution
Activators		Proprietary additives that enhance the amine solution's absorption rate or selectivity. Generally are included in FA, BA, and TA results
Water	Water	Water is essential for acid gas absorption.
Physical Properties	Density Viscosity Conductivity Surface Tension Appearance	Physical properties of the solution provide monitors of compositional changes in the amine solution that affect absorption, regeneration, heat demand, corrosivity, and equipment longevity.

Watch trends. When BA rises or TA+Water departs significantly from near 100%, further information is needed. The second tier analyses – for dissolved substances – are listed in Table 6.

Table 6 Dissolved Substances in Amine Solutions (other than Solvent Amine)		
<u>Type</u>	<u>Analytes</u>	<u>Description and Role</u>
Acid Gas (AG)	Rich Loading (RL) Lean Loading (LL) H ₂ S, CO ₂ , Acid Gas Loading (AGL)	Acid gas (H ₂ S & CO ₂) in the solution exiting the Absorber Acid gas (H ₂ S & CO ₂) in the solution exiting the Regenerator The acid gases measured separately; In amine solution are ionic: HS ⁻ , HCO ₃ ⁻ , CO ₃ ²⁻ , and carbamate ions.
Acids – organic and inorganic, also called Heat Stable Salts (HSS)	Heat Stable Salts (HSS); Total HSS; BA; HSAS; IHSS; individual anions*; ATB-RFB; Conductivity;	Acids which accumulate in the amine solution by absorption and chemical reactions within the amine solution. They reduce amine capacity, contribute to corrosion, increase density and viscosity and conductivity. Two general types: Weak Acid Anion (WAA) and Strong Acid Anions (SAA) (see Appendix A)
Acids – amino (AA)	Bicine; Total Amino Acids; BA	Amino acid derivatives of amines by reactions within the amine solution; may be included among HSS; Amino acids titrate as BA and as TA. Amino acids strongly enhance corrosion.
Cations, Inorganic, also called Strong Cations (SC)	Strong Cations (SC), e.g. K ⁺ , Na ⁺ ; Corrosion metal ions (Fe, Cr, Ni, etc) Inorganic HSS (IHSS)	Alkali cations which accumulate in the amine solutions from cooling water leaks or deliberate caustic addition; Corrosion metals result from aggressive acid gases, erosion, enhanced by HSS and amino acids
Basic Degradation Products (BDP)	Total Base (TB); Total Amine Base (TAB); Actual Total Base (ATB); Total Nitrogen (TN); TB-ATB; dimers (THEED, HEED, HEP, etc), ureas.	Amines and amine dimers that result from chemical degradation of the solvent amine; have some acid gas absorbing capacity. Amine dimers enhance corrosion
Neutral Degradation Products (NDP)	Amides, formylamines, Oxazolidones; Hydrolysables; Total Nitrogen (TN) ; TN-TB;	Non-ion results of chemical degradation of the solvent amine; Amides are in active reversible equilibrium with their corresponding organic acid HSS anion.

*HSS anions most commonly determined individually include formate, acetate, propionate, glycolate, oxalate, chloride, thiocyanate, thiosulfate, sulfate, and sulfite

The numerous analytes listed in Table 6 can be daunting. The several analytes shown within individual boxes of Table 6 may each show a different part, or overlap or even disagree with one another, requiring informed interpretation of the respective results. More of these are discussed below.

Many of the dissolved substance cause corrosion or enhance corrosion by attacking the protective iron sulfide layer. Iron carbonate can form protective layers, but most often creates suspended solids. Corrosion products create solids in the amine solution. Corrosion products along with other insoluble or semi-soluble substance create the third tier of analytical problems listed in Table 7.

Table 7 Insoluble, Partially Soluble or Dispersed Substances in Amine Solutions		
<u>Type</u>	<u>Analytes</u>	<u>Description and role</u>
Solids	Total Suspended Solids (TSS)	From corrosion products, chemical and physical; TSS contribute to further corrosion, flow restrictions, and plugging. TSS stabilize foam
Hydrocarbons	Total Petroleum Hydrocarbons (TPH)	TPH carryover from contact with petroleum gas or liquid. TPH may contribute to or inhibit foam.
Surfactants	Foaming Tendency, Break time, Foaming Potential; Surface Tension;	Polar/non-polar molecules that cause foaming. Typically in very low concentrations but have large physical effects inhibiting acid gas absorption and stripping. Surfactants cause system upsets and solvent losses
Antifoam	Si (confirm presence of silicone antifoams only); no direct analyses	Antifoam is deliberately added to reduce foaming; Note: excess antifoam can cause foam.

All of the contaminants in Tables 6 and 7 have their effects on the amine solvent performance and/or the amine system hardware. Contaminants can immediately change physical properties (density, viscosity, surface tension, thermal conductivity, electrical conductivity, foaming tendency) and the water content, which can influence film absorption and desorption rates. Longer term affects include corrosion, plugging, flow restriction, foaming, and inhibited processing rates. Given the importance of short and long term characteristic effects of these contaminants it is very important have regular analytical reports. But how does one make sense of them?

RECONCILING VARIOUS ANALYTICAL METHODS

When one compares reports from two different labs there may appear to be inexplicable differences in apparently the same analyte. Some of the confusion results from differences in terminology and some from differences in lab procedural definition of analytes of the same name. For example, the question “What is the Heat Stable Salts content of this sample” could have the following CORRECT answers:

Heat Stable Salt Anions	14609	ppm(m)
Total Heat Stable Salts	3.13%	as DEA
HSAS	1.49%	as DEA
IHSS	1.63%	as DEA
Total HSS/Total Amine	11.14%	of DEA
	0.1114	mol/mol

From 1.5 to 11 %! No wonder we are confused! Notice the importance of the prepositions “as” and “of” which are often not included in conversation or reports. We prefer the first two in the above list, because they are direct expressions of the two parts of the Total Heat Stable Salts: the anions and the amine equivalent cations. The others have good utility, however, and need to be understood.

In the next table (Table 8), we attempt to reconcile the differences and show how one can translate various reports to a common basis. The “Really is” column uses terms defined herein (bold-face items in Tables 5, 6, and 7). The “Method Description” column provides information you can use to help your chemist tell you which analyte really is on the analysis report. Similar analytes are grouped together in the table.

<u>Reported as</u>	<u>Really is</u>	<u>Method Description</u>	<u>Comments</u>
Free Amine (FA) or Regenerable Free Base (RFB)	Free Amine (including BDP)	Titration of sample as received with HCl, tracked by pH or Conductivity to calculate correct endpoint	Reliable FA if correct endpoint. Must subtract free OH ⁻ in rare cases that it is significant
Free Amine (FA) or Regenerable Free Base (RFB)	Free Amine + WAA	Titration of sample as received with HCl with colorimetric or dead-stop pH endpoint	Overestimate FA UNLESS no WAA present. Must subtract free OH ⁻ in rare cases that it is significant
Total Amine (TA)	Total Amines (including BDP)	TA titration: Over-acidify sample, (nitrogen) purge acid gas, titrate with NaOH to excess, tracking pH or Conductivity to calculate correct endpoints for amine	Reliable TA, if endpoints are correctly chosen. BDP can have 2x contributions if subtle endpoint is not considered.
Total Amine (TA)	BA + FA	Add results of FA and BA titrations	Not as accurate as the TA titration (see BA and BA observed)
Alkalinity	FA	(see Free Amine)	(see Free Amine)
Amine by GC	Total solvent amine	Gas Chromatography peak(s) specific to the intended amines in the solvent.	Excludes BDP, so comparison to TA can reveal BDP. For formulated amines only the amine supplier can determine this.
Amine by IC	Total solvent amine	Ion Chromatography peak(s) specific to the intended amines in the solvent.	(see GC amine)
Amine Balance	BDP estimate	Titrated TA minus IC- or GC-identified solvent amine	If >0, BDP may be present; if <0, faulty analysis
Nitrogen	Total Nitrogen (TN)	Elemental analysis of nitrogen in the sample. Using Amine molecular weight, calculate TN as amine.	

<u>Reported as</u>	<u>Really is</u>	<u>Method Description</u>	<u>Comments</u>
Nitrogen Balance	NDP estimate	TN - TA	If >0, NDP are present. If <0, amines of higher molecular weight than assumed are present or TA is wrong.
Degradation Products, itemized (HEED, HEI, THEED, HEP, formylamines Oxazolidones, etc)	BDP and NDP species	HPLC and GC analysis calibrated for specific degradation products	The best way to determine what and how much BDP or NDP are present. GC requires derivitization to avoid errors from on column degradation.
nFDEA, FDEA, DEAF, FDIPA, DIPAF, FMEA, etc	Amides, formylamines (part of NDP)	HPLC or GC (with derivitization)	(see BDP and NDP) Only in primary and secondary amines (MDEA and TEA cannot form amides); active equilibrium with formate salts
Hydrolyzables	Amides + idones (Total NDP)	Hydrolysis in excess base and heat and measure the acids produced by the hydrolysis. Calculate amides from WAA HSS produced and Oxazolidones from CO ₂ produced	A good check on recovery of HPLC and GC species analyses. Heavier amides are detected
Acid Gas Loading (AGL)	AGL by BA change	BA before – BA after boiling	Detects H ₂ S and CO ₂ , but approximate because boiling does not expel all AG from all amines
Acid Gas Loading (AGL)	AGL by charge balance	BA observed + Strong Cations – Total HSS	OK if no amino acids are present and HCO ₃ ⁻ /AGL are small.

<u>Reported as</u>	<u>Really is</u>	<u>Method Description</u>	<u>Comments</u>
H ₂ S or Acid Gas Loading (AGL)	H ₂ S	Titration of Sulfide by AgNO ₃ ; direct titration of amine sample diluted in water.	Most reliable H ₂ S method; can detect mercaptans separately; Doesn't detect CO ₂ so may not be total AGL.
H ₂ S or AGL	H ₂ S + S ₂ O ₃ ⁼ + SO ₃ ⁼	Titration of excess Iodine with sodium thiosulfate after addition of amine sample to acidic Iodine	False high H ₂ S results if thiosulfate HSS are present
Acid Gas Loading (AGL)	H ₂ S + CO ₂	Sum of direct measure of H ₂ S and CO ₂ individually. Best if H ₂ S by AgNO ₃ titration and CO ₂ by TIC	Most reliable AGL. When translated to mol AGL/mol Amine can give false low impression of amount amine involved if CO ₃ ⁼ is present.
Acid Gas Loading (AGL)	AGL/FA	(H ₂ S + CO ₂)/FA, mol/mol	Most common expression of LL and RL
Acid Gas Loading (AGL)	AGL/TA	(H ₂ S + CO ₂)/TA, mol/mol	Similar, but not identical to AGL/FA. Differs by the factor FA/TA
CO ₂	CO ₂ (approx.)	Add BaCl ₂ (hot), titrate BaCO ₃ precipitate with HCl	<u>Poor</u> accuracy and repeatability in amine solutions
CO ₂	CO ₂	Total Inorganic Carbon (TIC): Instrument that automates the acidification of the sample, trapping the released CO ₂ gas and the coulometric titration; removes H ₂ S before titration	The only reliably accurate method for CO ₂ in all amine solutions

<u>Reported as</u>	<u>Really is</u>	<u>Method Description</u>	<u>Comments</u>
HSS, Total HSS, or HSS by titration	Total HSS	After removing amine, strong cations and amino acids by cation exchange, titrating with base (NaOH or KOH) and determining endpoints by inflexion points in pH or conductivity	Detects all HSS anions. Excludes amino acids. High thiosulfate is under-reported. Can determine Weak Acids and Strong Acids as separate groups if use conductivity. Estimate amides from WAA.
HSS	HSAS	Boil sample to remove LL, titrate with base (NaOH)	LL incompletely removed from many amines, so may give high estimate of HSAS
HSS	Total HSS (unless SC present)	Over-acidify sample, purge acid gas, then titrate with NaOH to excess, tracking pH or Conductivity to find correct endpoints. Calc HSS by difference of much larger numbers.	Poor accuracy except for large (>5 wt%) HSS and zero SC. Purging of AG by boiling could lose Formate HSS: use N2 or air. WAA endpoint is weak if by pH.
HSS	HSS species	Sum of HSS anions determined individually by Ion Chromatography	Reliable for anions reported. Not all possible anions are known, so HSS species is typically less than Total HSS. Some labs include bicine, others don't.
Strong Acid Anions	HSS species	Sum of all HSS anions determined individually by Ion Chromatography	(See "HSS species"). "Strong acid" here means "stronger acid than the Acid Gases". Thus it means SAA + WAA.

<u>Reported as</u>	<u>Really is</u>	<u>Method Description</u>	<u>Comments</u>
Strong Acid Anions (SAA)	HSS species, Anions of Strong Acids only (SAA)	Sum of the Strong or “polarizable” anions determined individually by Ion Chromatography	Include chloride, thiocyanate, sulfate, thiosulfate, nitrate, oxalate, sulfite, bromide, phosphate, arsenate (anions of stronger acids than formic acid)
Strong Acid Anions (SAA)	Anions of Strong Acids (SAA)	From the Total HSS titration, the Strong Acid section. Clearly discernable with conductivity; difficult to discern with pH (see Appendix A). Sample prep by cation exchange trades the counter cation (AmH^+ or Na^+ or K^+) for H^+ which is then titrated with base (NaOH)	SAA do not consume H^+ when titrated with acid. Accurately detected as a group by this procedure
Weak Acid Anions (WAA)	Anions of Weak Acids (WAA)	From the Total HSS titration, the Weak Acid section. Clearly discernable with conductivity; difficult to discern with pH (see Appendix A) Sample prep by cation exchange trades the counter cation (AmH^+ or Na^+ or K^+) for H^+ which bonds with WAA, then is titrated away again with base (NaOH)	WAA consume H^+ (making an acid molecule). Accurately detected as a group by this procedure.
Weak Acid Anions	HSS species, Anions of Weak Acids only (WAA)	Sum of the Weak Acid anions determined individually by Ion Chromatography	Include formate, acetate, propionate, butyrates, glycolate
HSAS or BA	BA observed	Titrate sample as received with base (NaOH)	Includes amino acids (more than bicine) and LL plus HCO_3^- again. Reliable when CO_2 is small relative to BA.

<u>Reported as</u>	<u>Really is</u>	<u>Method Description</u>	<u>Comments</u>
HSAS or BA	BA	BA corrected = BA observed minus extra HCO_3^- contribution, calculated by charge balance: $\text{LL} + \text{HSS} - \text{Strong Cations}$.	Actual AmH^+ in solution as received. Can be used in mass balance where amino acids are itemized separately. Estimate HCO_3^- correction from TIC, pH, and Ka_2
HSAS	HSAS	Total HSS – IHSS or Total HSS – Strong Cations	Generally reliable; Accuracy depends on Total HSS accuracy
HSAS	HSAS	HSS Species – IHSS or HSS Species – Strong Cations	May underestimate (see HSS Species)
HSS neutralized	SC/TotalHSS	Calculation: fraction of TotalHSS that are IHSS: expressed as fraction or %.	Helps avoid excessive caustic. Best close to zero; can cause LL rise if exceeds 0.6 (60%)
$\text{S}_2\text{O}_3^{=}$ HSS	$\text{S}_2\text{O}_3^{=} + \text{SO}_3^{=} + \text{H}_2\text{S}$	Titration of excess Iodine with sodium thiosulfate after addition of amine sample to acidic Iodine	False high thiosulfate if H_2S is present
Chloride (Cl^-) HSS	Chloride (Cl^-) (one HSS species)	Titration of Cl^- by AgNO_3 after acidification of amine sample in water, (nitrogen) purging of acid, and iodine oxidation of any $\text{S}_2\text{O}_3^{=}$.	Very reliable chloride measurement, even to < 20 ppm with large sample.
Thiocyanate (SCN^-) HSS	Thiocyanate (SCN^-) (one HSS species)	Titration of SCN^- by AgNO_3 by same procedure as titration of Cl^- .	Very reliable SCN^- measurement, but will include any Bromide if present. (e.g., sea or ground water contamination)

<u>Reported as</u>	<u>Really is</u>	<u>Method Description</u>	<u>Comments</u>
Strong Cations	Strong Cations	“Strong Cations Titration”: Anions (AGL and HSS) in the amine sample are replaced by OH ⁻ by anion exchange. Any AmH ⁺ is neutralized to FA and H ₂ O, leaving all Strong Cations with an OH ⁻ companion anion. The OH ⁻ is then titrated with acid, equaling the Strong Cations.	Excellent accurate determination of the Strong Cation characteristic in amine solutions,
Na ⁺ , K ⁺ , Ca ²⁺ , Mg ²⁺	Strong Cations	ICP or IC measurement	ICP accurate; IC may have interference from amines for K ⁺
Strong Bases	Strong Cations	Determined by ICP, IC, calculated to wt% as amine	Another name for Strong Cations or IHSS
Ash	Strong Cations	After burning the sample in a furnace, weigh the amount of ash remaining, report as wt% ash in the sample. Three varieties possible: sulfated ash, carbonate ash, oxide ash	Typically interpreted as Na ash, but includes all metal cations present. Na ≈ sulfated ash/3.1, carbonate ash/2.3, Na ₂ O/1.4
IHSS	Strong Cations	Sodium and Potassium by ICP, IC, or Strong Cations Titration, then calculate the equivalent amount of amine; report as wt% as amine	Assumes all strong cations have HSS anion companion. Reported as amine wt% for direct comparability with HSAS and Total HSS
Bicine	Bicine	Amino Acids analysis by Ion Chromatography	Accurate if carefully calibrated and run with check standards.
Amino Acids, total	Total Amino Acids by IC	Amino Acids analysis by Ion Chromatography, bicine standardization applied to peaks with retention times ___ to ___ times the bicine retention ratio	Good approximation; check against Total Amino Acids by charge balance

<u>Reported as</u>	<u>Really is</u>	<u>Method Description</u>	<u>Comments</u>
Amino Acids, total	Total Amino Acids by charge balance	Amino Acids = BA observed – Total HSS – AGL - HCO ₃ ⁻ + Strong Cations	Good approximation, better if HCO ₃ ⁻ is insignificant. Assure moles and equivalents are correctly applied
Petroleum Hydrocarbons or TPH	TPH (IR)	Infrared measurement: Acidified sample is extracted in tetrachloroethylene, then Infrared absorbance is measured	Acidification is a MUST. Sampling procedures are critical. In the lab must assure uniform dispersion of hydrocarbons before and during sampling.
Petroleum Hydrocarbons or TPH	TPH (GC)	GC measurement: Acidified sample is extracted in tetrachloroethylene or toluene, then injected in Gas Chromatograph. Integrate specified range of retention times.	Acidification to pH <3 is a MUST (major errors have occurred by not excluding amine). Sampling (see TPH (IR))
TSS	TSS	Large sample (50 to 100 g) is filtered through 1 micron filter. Mass of solids on filter is determined. Calculate mg solids per L solution.	Large relative error possible because of small mass of solids. Sampling technique is critical (see TPH)
TSS by absorbance	turbidity	Transmittance of 810 micron wavelength light compared to clean solvent. Reduction in transmittance due to scattering of light by particles.	Quick easy test, good for tracking gross trends or filter effectiveness. Can roughly calibrate against TSS for short range of concentrations and uniform particle size distribution.

Glossary of Analytical Terms

Table B-1, Appendix B, presents the basic definitions of terms and abbreviations commonly used in amine analysis reports, sorted alphabetically. Some comments about measurements are included. See Table 8 for more complete operational comparison of analysis methods.

SOME QUESTIONS TO ASK THE ANALYST/CHEMIST TO ASSURE THE MEASUREMENTS ARE CLEAR AND UNDERSTOOD

1. Sampling
 - a. Was the dead leg flushed before taking the sampling?
 - b. Record the actual unit conditions when the samples are taken. Is there a plant upset or unique operating conditions?
 - c. Trouble shooting
 - i. Are you intentionally taking non-routine samples? Record the reason for the sample to help trouble shooting.
 - ii. Taking samples up stream and down stream of filters and activated carbon beds to discover performance issues.
 - iii. Up stream and down stream of heat exchangers to spot leaks in the heat exchanger.
2. Making sure Free Amine (FA) or amine strength measurement is correct: how much amine is available for acid gas adsorption?
 - a. Is it a titration with acid? If yes, good.
 - b. Is the endpoint of the titration determined by inflection points in a conductivity or pH curve? If yes, good.
 - c. Is the endpoint determined by color indicator? If yes, worry about accuracy.
 - d. Is the endpoint determined by “dead-stop” at a specified pH? If yes, worry about accuracy.
 - e. Spiking with Acetic Acid before titration can help get more accurate endpoint for FA.
3. Understanding total amine (TA) test
 - a. How total amine test is done (GC, titration, other)?
 - i. If GC, ask what amines are quantified and are there noteworthy not quantified / unidentified peaks.
 - ii. If titration, ask if basic species like amino acids or piperazine are subtracted from the reported total amine number. If the number is reported as titrated, the total amine number is actually a total base number.
4. Making sure HSS is correct
 - a. How HSS measurement is made (IC or titration)?
 - i. If IC, the individual analysis of species should be available. See if the common anions are analyzed for; i.e. Formate, acetate,

propionate, glycolate, oxalate, chloride, thiocyanate, thiosulfate, sulfate, and nitrate.

- ii. If titration,
 1. Is a direct titration of the amine sample with base? If so, the result is BA.
 2. How is Lean Loading (AGL) removed? If boiling of direct sample, worry about false high result.
 3. How are strong cations removed before analysis or how is their affect accounted for in the final HSS result? Caution: some acidification and back-titration methods detect WAA HSS (not SAA HSS) and detect only the strong cations which exceed the equivalent of the Total HSS. Such methods estimate HSAS, not Total HSS. .
5. Understanding Cation Test results.
 - a. How are Strong Cations (Sodium, Potassium, Calcium, etc.) determined?
 - i. If by IC or ICP,
 1. Was the signal within the calibration range?
 2. Are there any false highs due to interferences (such as amine with K^+ in IC)
 - ii. If by titration:
 1. Was sufficient strong base anion exchange resin used to absorb all the LL and HSS anions (at least 2 times the equivalent)?
 2. Has the titration been checked against ICP or IC for this amine system? (It is a good check on endpoint determination technique. Rarely, but it has happened, the titration method will grossly exceed the actual strong cations concentration for unknown reasons)
 3. Only strong alkali and alkaline earth metals are detected by titration
6. Corrosion metals by ICP or AA
 - a. Filtered or digested metal (dissolved or total metals)? Dissolved metals are the desired result. High dissolved metals in lean amine samples indicates presence of HSS, amino acids, and/or polymeric amines (BDP)
 - b. Sample preparation of ICP samples, especially for solutions that contain solids, will affect the results. If the sample is just filtered before the digestion of the liquid sample, then the measurement is of only the dissolved metals.
 - c. If the samples are not filtered until after acid digestion then the metals in the solids are included metals report. Generally it is more instructive to determine the metals in the filtered solids separately from the liquid.
7. Mass Balance or "Residue" calculations
 - a. Do we have a water content analysis by Karl Fischer Titration? If not, don't even try the calculation.

- b. Relies on accurate Total Amine (see above), correct molecular weight of the amine(s), accurate analysis of water and AGL, and of all analytes included in the calculation.
 - c. Can indicate that there are contaminants present that have not been analyzed.
 - d. Can show errors in measurements especially water and amine measurement.
8. Ask for outside lab testing for trouble shooting
- a. If your lab does not measure water content, then sending out for a water measurement will help with mass balance, checking other measurements, and assuring your amine system is meeting your water content specification.
 - b. Complete analysis by outside lab should be done at least annually, more often if contaminants are growing or changing. Remember HSS, amino acids, and BDP contribute to corrosion and can cause severe damage.

WHAT OPERATIONS-SIGNIFICANT INFORMATION IS REVEALED BY ANALYSIS OF CONTAMINANTS?

Here are some examples.

Table 10 Analytical Symptoms of some Amine System problems	
<u>Symptom</u>	<u>Possible Interpretations</u>
FA decreasing	<ul style="list-style-type: none"> - Amine losses (carryover, entrainment, valve error, etc) - Water purge out of balance (total solution volume increasing) - HSS ingress - NDP forming: amides, if primary or secondary amine; oxazolidones if in high pressure CO₂ service
Total HSS increasing	<ul style="list-style-type: none"> - HSS ingress - Water content decreasing - Corrosivity increasing - Need HSS removed
FA increasing while BA increasing	<ul style="list-style-type: none"> - FA analysis error: FA report includes Weak Acid HSS
LL rise with no change in operating conditions	<ul style="list-style-type: none"> - Greater AG load in absorbers - Strong Cations ingress into solvent.
Total HSS > BA	<ul style="list-style-type: none"> - Caustic ingress or addition - Cooling water leak into amine solution
BA > Total HSS	<ul style="list-style-type: none"> - Amino Acids present (not included in Total HSS) - BA includes high LL
Thiosulfate HSS	<ul style="list-style-type: none"> - Oxygen ingress - SO₂ break-through (Claus Tail Gas)
Bicine (and other amino acids)	<ul style="list-style-type: none"> - Oxygen ingress (gas plants) - O₂, SO₂ and/or S₂O₃⁻ attack (refinery)
Strong Cations	<ul style="list-style-type: none"> - Caustic addition - “amine slops” added to amine and included some caustic - Cooling water leak into amine - “hidden” HSS - foaming tendency increasing (soaps)
Formate HSS	<ul style="list-style-type: none"> - Caused Cyanide or Carbon Monoxide ingress - If primary or secondary amine, Amides increase as Formate increases so Total Amine and Free Amine reduced => apparent amine loss, but it can be recovered (don't throw it away)

Table 10 Analytical Symptoms of some Amine System problems	
<u>Symptom</u>	<u>Possible Interpretations</u>
Acetate HSS	- Acetonitrile ingress - Oxygen ingress
Thiocyanate (SCN ⁻) HSS	- Cyanide reacting with H ₂ S
Chloride HSS	- Cooling water leak - HCl ingress
Solids (TSS) rising	- Corrosion - filters inadequate or spent
TPH	- Hydrocarbon carry-over into amine: inadequate knock-out drum
“Residue” increasing, but BA not	- Caustic ingress or addition - Cooling water leak into amine solution - Amine chemical degradation

CLOSING SUMMARY

In tables and text we have attempted to show both the simplicity of the amine system and the complicated array of contaminants that pollute amine solutions and cause problems for amine system function and longevity. The even larger array of analytical methods employed to determine contaminant concentrations in amine solutions expands the confusion. While there is some duplication among the tables, each provides a different perspective and thus can possibly provide aid to different people in the variety of situations amine systems present to focus on the analytical methods and data that are most instructive for the need at hand.

The fundamental focus must be on the following, which can be tracked with relatively few well selected analytical methods:

Free Amine (FA)

Total Amine (TA)

Bound Amine (BA)

H₂S

CO₂

The most likely contaminants can be determined with the same auto-titrator used for FA, TA, BA and H₂S:

Total Heat Stable Salts (HSS), including **WAA and SAA** estimates from conductivity titrations;

Strong Cations (SC)

Chloride

From the above, estimates can be calculated of the most common degradation products

Amino Acids (AA)

Amides (part of the NDP)

A specialized titrator (“Karl Fischer”) is needed to determine
Water

These analyses, from FA to Water, are the most important analytical parameters to have frequently and current at your fingertips.

From all the above, a mass balance or residue calculation yields an estimate of
Basic Degradation Products (BDP) + Neutral Degradation Products (NDP)

Add instrumental analysis methods for

Total Nitrogen (TN)

Amine species by GC or IC

HSS species by IC

Then by “amine balance” and “nitrogen balance”

BDP

NDP

Estimates might be segregated. These can be supported by HPLC or possibly GC identification of
specific BDP and NDP species.

Along the way,

Total Suspended Solids (TSS)

Total Petroleum Hydrocarbons (TPH)

Foaming Tendency

Foam break time

Density

pH

Conductivity

Viscosity

Surface Tension

can provide valuable clues to amine solution health.

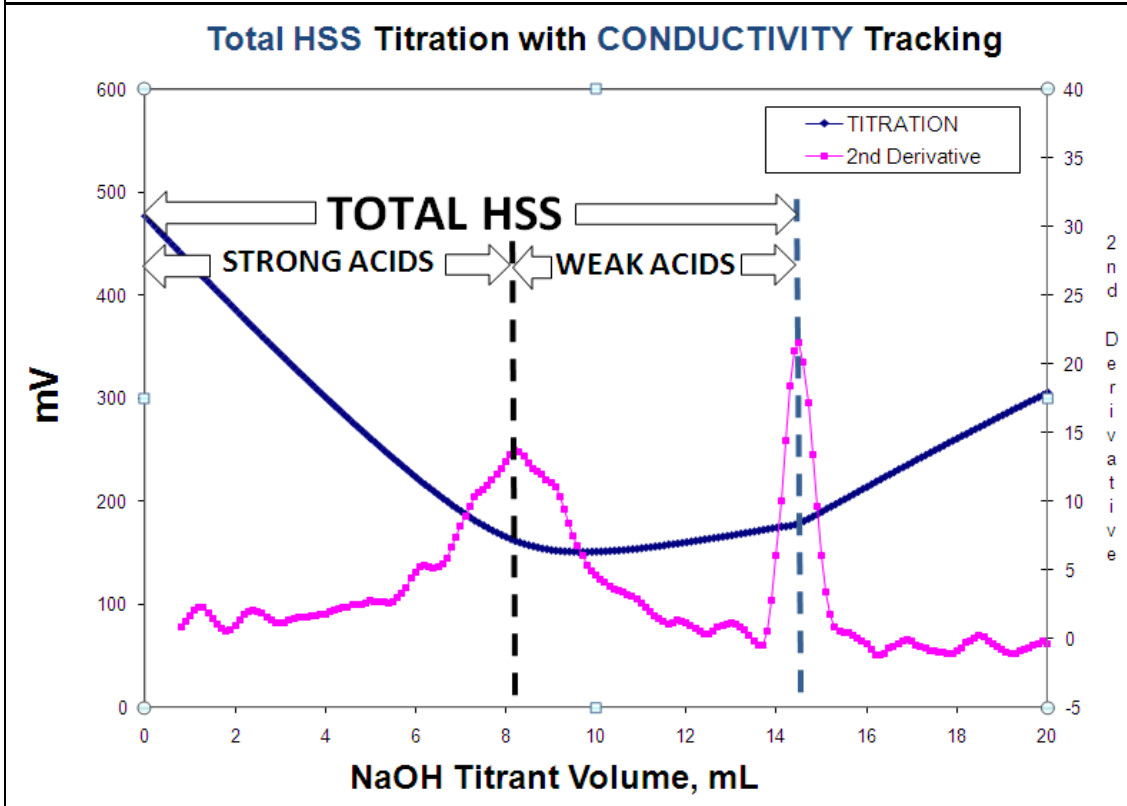
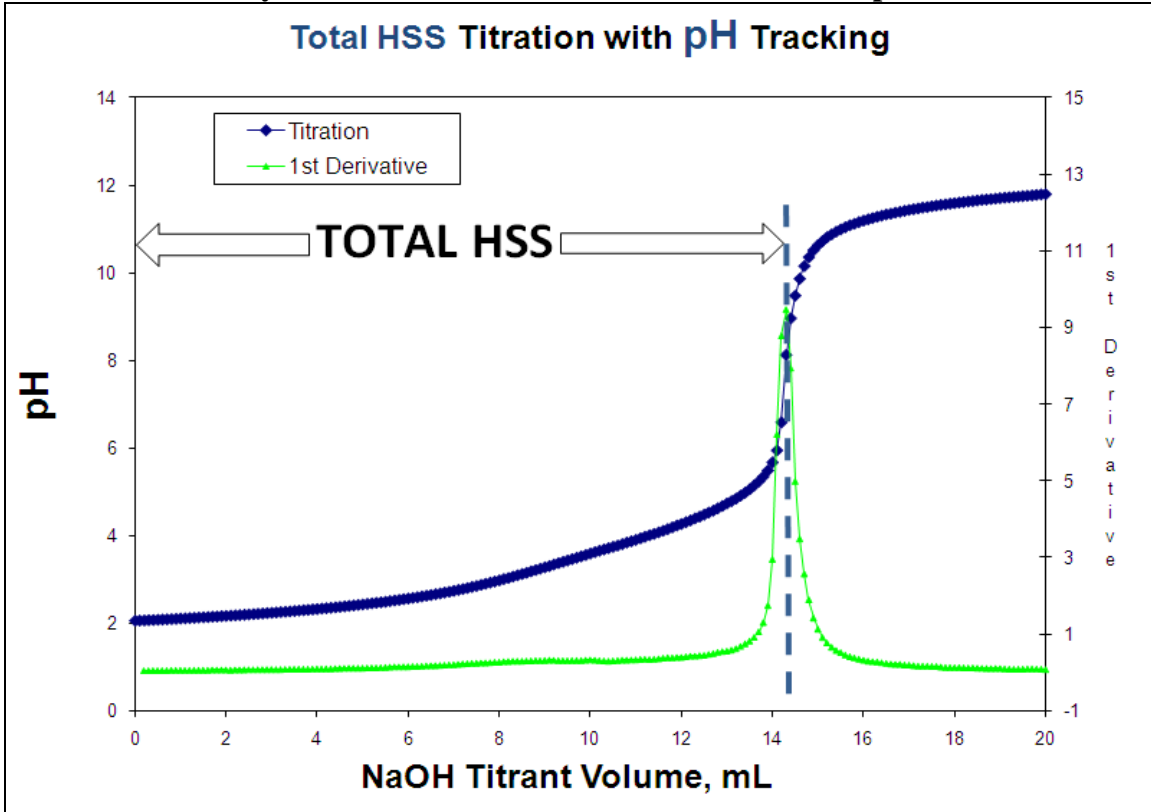
Tracking and graphing various data over long periods of time makes it easier to spot trends, gain a sense for normal analytical/sampling variability, recognize possible errors, key in on unexpected results, and track cause and effect on unit operations.

A plant needs to have locally only and automatic titrator, conductivity meter and probe, pH meter and probe, sulfide ion selective electrode and reference electrode, CO2 analyzer, and Karl Fischer titrator in order to provide the most important analyses. The other analytes can be done monthly, quarterly, or as needed by your company’s central analytical lab, amine vendor, or reclaimer.

TRADEMARKS FOOTNOTES

- DGA® is a registered trademark of Huntsman corporation

Appendix A
Conductivity Titrations Provide More Information than pH Titrations



APPENDIX B
GLOSSARY OF AMINE ANALYTICAL TERMS
(Alphabetical by Term)

Table B-1. Analytical Definitions and Measurement comments	
<u>Term</u>	<u>Definition</u>
acetate	Acetate ion, one of the HSS anions; a WAA; determined by IC.
AG	Acid Gases H ₂ S and CO ₂ . HCN is also an acid gas, but is rarely determined, because it typically reacts in amine solutions to become formate or thiocyanate HSS.
AGL	Acid Gas Loading, the AG concentration in an amine solution
Alkalinity	(see FA [Free Amine])
Amine Balance	Amine balance is Total Amine (TA) by titration minus the identified amine by Gas Chromatography or Ion Chromatography. If positive, BDP are present; if negative, faulty analysis.
Amine by GC	Amine measured by GC (Gas Chromatography) The difficulty with the GC method it will only measure the specific amine(s) you are looking for and other basic species in the amine may not be detected or reported.
Amine, primary	[see Primary Amine]
Amine, secondary	[see Secondary Amine]
Amine, tertiary	[see Tertiary Amine]
Amino Acid (AA)	A molecule with an amine nitrogen attached to a carboxylic acid group. A common degradation product in alkanolamine solutions, detectable by a specific IC amino acids method. Bicine and HES have been specifically measured in amine solutions. Total amino acids can be approximated from Bicine, HES, and other unidentified peaks in the chromatogram, or from Bound Amine titration.
Appearance	The appearance of the solution can give clues to difficulties present in the amine system. Particles are indication of corrosion/erosion in the system. Color indicates dissolved or suspended contaminants. An emerald greenish color can be due to extremely small (colloidal) iron sulfide particles in solution. Hydrocarbons can be visually observed. If the odor detection is done carefully, one can detect contaminants like hydrocarbons, or unplanned high sulfide lean loading.
ATB	Actual Total Base = Free amine or RFB + base bound to other acids. Depending on measurement may be the same as TB or Total Amine Bases (TAB).
BA	Bound Amine – Amine that <u>cannot</u> participate in acid gas adsorption because it has already reacted with an acid and is bound to a Hydrogen Ion (H ⁺); also designated by AmH ⁺ . It rises as HSS and/or AGL rise.
BDP	Basic Degradation Products: amines and amine dimers that result from chemical degradation of the solvent amine; have some acid gas absorbing capacity. Amine dimers enhance corrosion.

Table B-1. Analytical Definitions and Measurement comments	
<u>Term</u>	<u>Definition</u>
Bicine	An Amino Acid found in amine solutions (primarily MDEA and DEA) now routinely determined by IC amino acids method. In some reports, included in HSS species; in other reports, treated separately from HSS. pKa very close to that of MDEA, so is indistinguishable from amines in acid/base titrations.
butyrate	Butyrate ion, one of the HSS anions; a WAA; determined by IC, but rarely found; strong positive interference by CO ₂ .
Cl ⁻	Chloride ion, one of the HSS anions, a SAA; determined by AgNO ₃ titration or by IC.
CO ₂	Carbon dioxide, an acid gas (AG), absorbed in amine solution with aid of acid/base reaction or CO ₂ addition to a primary or secondary amine, resulting in HCO ₃ ⁻ (bicarbonate), CO ₃ ⁼ (carbonate), and/or AmCOO ⁻ (carbamate) ions.
Conductivity	Electrical conductance of the solutions. As ionic contaminants (including AGL) increase in the solution, the conductivity increases. Thus conductivity is useful for showing contaminant trends within a system, but not for determination of actual contaminant concentration. This is a conductivity meter measurement and normally reported as milliSiemens.
DEAF	DEA formamide = FDEA, an NDP [see Formyl Amines]
Density	Density is mass per unit volume of solution, reported as g/mL. The density of the amine solution rises with increasing salt contamination in the solution. A correlation can be made between density and HSS concentration if all other components are nearly constant, but water, amine, degradation products, and HSS concentration affects density.
DIPA-F	DIPA formamide = FDIPA, an NDP [see Formyl Amines];
Distillation Residue	The remains of a vacuum distillation procedure. Intended to be a measure of Residue ₂ , but may include bound amine and some acid gas, thus may be an overestimate of all contaminants.
FA	Free Amine is amine in its free base state. Can be also called Regenerable Free Base (RFB) or usable amine. It can be measured by titration with acid. Reported as wt% using the molecular weight of amine. It can also be calculated from FA = TA – BA. The colorimetric titrations or dead stop endpoint titrations may report higher than the actual FA if WAA are present.
FDEA	formylDEA, an amide of DEA, an NDP [see Formyl Amines]; in active reversible equilibrium with DEAH ⁺ and formate ⁻
FDIPA	formylDIPA, an amide of DEA, an NDP [see Formyl Amines]; in active reversible equilibrium with DIPAH ⁺ and formate
ferrocyanate	Ferrocyanate ion, a cyanide complex of iron, one of the HSS anions; a WAA; determined by combination of AgNO ₃ titration and IC data. It is believed that CO complexes of iron exhibit the same analytical behavior.
Foam Break Time	The time (in seconds) for the foam to break. Normally break times longer than 10 seconds can lead to problems in a amine system due to residence time on trays

Table B-1. Analytical Definitions and Measurement comments	
<u>Term</u>	<u>Definition</u>
Foam Height/ Foam Tendency	It given as mL on the graduated cylinder or height above the liquid level. Interpreting results is different for different methods. Difficult to compare between testing methods. The tests are generally more qualitative than quantitative. Normally less foam height is better for amine systems.
Foam Tests	Can be a simple qualitative shake test or a gas purged through the amine solution in a graduated cylinder for quantitative evaluation. Matching the foam test results to the foaming behavior in an absorber or regenerator tower is extremely difficult, because temperature, pressure, and gas bubble size rarely match. Foaming causing compounds, surfactants, at very low (under 100 ppm) cause foam that can severely hamper absorber and stripper tower operation. Obtaining a representative sample of surfactant in amine is difficult both at the plant and at the lab. Sampling greatly affects the results of the test and how meaningful it is to the system operation.
Foaming Potential Rating	Break time and foam height are combined in the von Phul equation to give an indication of how likely a system is to have foaming problems, using a scale of 1 (no problem) to 10 (need intervention).
formate	Formate ion, one of the HSS anions; a WAA; determined by IC.
Formyl Amines and other Amides	Primary and secondary amines undergo a water elimination equilibrium reaction with a formic acid (or any organic acid) to form an amide, an NDP. The amide reduces available amine for acid gas adsorption and hides the acid, which would otherwise appear as an HSS. Have been called <i>dormant HSS burden</i> because they will revert <i>back to amine</i> and acid when HSS anions are removed by ion exchange. To offset the reduced amine solution capacity caused by amide formation, more amine is added or water content is reduced. Formylamines (from formic acid and amine) are normally measured by liquid chromatography (HPLC) or gas chromatography (GC). Total amides are measured by hydrolysis.
GC	Gas Chromatography, an instrumental analysis method for determining amine species, and some BDP and NDP
glycolate	Glycolate ion, one of the HSS anions; a WAA; determined by IC.
H ₂ S	Hydrogen sulfide, an acid gas (AG). Absorbed in amine solution with aid of acid/base reaction resulting in HS ⁻ (bisulfide) ion.
HEED	hydroxethylethylenediamine, a BDP of MEA
HEOD	Hydroxyethyloxazolidone: the oxazolidone of DEA, an NDP of DEA
HEP	1,4-bis(hydroxethyl)piperazine, a BDP of DEA
HES	Hydroxyethylsarcosine, an Amino Acid found in amine solutions now routinely determined by IC amino acids method.
HPLC	High Performance Liquid Chromatography, an instrumental analysis method for determining BDP, NDP, and some amine species
HPOZD	Hydroxyisopropyloxazolidone: the oxazolidone of DIPA, an NDP of DIPA

Table B-1. Analytical Definitions and Measurement comments	
<u>Term</u>	<u>Definition</u>
HSAS (or AHSS)	Heat Stable Amine Salt – A heat stable salt that is made up of an amine molecule and anion. The number is best calculated by $HSAS = Total\ HSS - IHSS$ and not measured directly. It is expressed as wt% as amine using the amine molecular weight. It may also be calculated as BA - AGL.
HSS (total)	<p>Heat Stable Salts (total) - A salt in the alkanolamine (amine) solution that is not affected by heat. The heat stable salt does not regenerate in the regenerator and remains in the circulating amine system. HSS (total) can be accurately measured by a titration procedure which prepares the sample with cation exchange resin. HSS are over- or under-reported by titration procedures that detect Bound Amine or involve over-acidification (without ion exchange) of the amine sample before titration.</p> <p>Individual HSS anions can be measured by Ion Chromatography (IC). The thus identified HSS anions are summed to provide a total HSS. In general, Total HSS by titration should be the same or larger than Total HSS by IC (HSS species). One exception is if significant thiosulfate is present, the titration method gives a false low HSS concentration and IC must be relied upon.</p> <p>HSS reports can be confusing, first, because the various measurement methods provide different answers, and, second, because of units of measure employed in the reports. Most often HSS will be reported as the wt% of the equivalent amount of amine. This means, for example, if HSS concentration were 1 mole/kg of solution, it would be 10.5 wt% as DEA, 11.9 wt% as MDEA, 6.1 wt% as MEA, 13.3 wt% as DIPA, etc., etc..</p>
HSSB	Heat Stable Salt Burden- Total HSS plus amides (e.g. fomylamines). HSSB recognizes that amides are in active equilibrium with their corresponding HSS anion and amine, and are “hidden” HSS. When seeking HSS incursion rates, must base on it HSSB.
IC	Ion Chromatography, an instrumental analysis method for determining HSS anions, Strong Cations, amino acids, and amine species
IHSS	Inorganic Heat Stable Salt – A heat stable salt that is made up of a metal cation and an anion, however it typically reported in units of wt% as amine. It is assumed all of the cationic metals present form IHSS. This is calculated from the measured molar concentration of metal cations present in the sample.
Lean Loading (LL)	Lean loading is the amount of acid gases ($CO_2 + H_2S$) in the lean amine. This indicates the quality of the amine stripping. CO_2 is measured by coulometric titration. H_2S is measured by potentiometric titration. Reported as ppm or wt% as CO_2 and H_2S , respectively, or as mol/mol amine. The low molar loading is often important to meeting the specification on the gas.
LL	Rich Loading, the AGL in an amine solution exiting the regenerator (stripper)

Table B-1. Analytical Definitions and Measurement comments	
<u>Term</u>	<u>Definition</u>
Mass Balance	Total percentage of measure solution components and contaminants. It is helpful in spotting unaccounted for contaminants. The calculations can be sensitive to the molecular weight used and care is necessary not to count some species twice. It may not be possible to measure, identify and quantify all solvent components and contaminants. Total Amine+water+AGL +HSS anions +Cations+amino acids + BDP+NDP = Mass Balance
Metals	Cation species can be identified by IC and ICP or AA. Include Strong Cations and corrosion products. Expressed as ppm of each metal ion. This has the advantage of identifying the species present.
NDP	Neutral Degradation Products: non-ionic results of chemical degradation of the solvent amine; include amides and oxazolidones; amides are in active reversible equilibrium with their corresponding organic acid HSS anion [see Formylamines and other amides]
Nitrogen Balance	Total nitrogen measurement minus nitrogen calculated from TA titration. If positive, excess nitrogen could be from SCN- (a HSS anion), polymer BDP and/or NDP. If negative, faulty analysis or wrong MW for the amine
Oxalate	Oxalate ion, one of the HSS anions; a SAA; determined by IC.
Oxazolidone	Degradation product (NPD) of primary and secondary alkanolamines with CO ₂ , creating an N-C-C-O-C- ring structure; formed by dehydration of the carbamate.
OZD	2-oxazolidone, specifically, the oxazolidone of MEA
pH	As BA increases the pH decreases. This is a pH meter measurement. The pH is dependant upon amine concentration and amine type. It is not suggested to quantify contaminants by the pH measurement. In general, the primary and secondary amines are stronger bases than the tertiary amines, run higher pH in lean and have higher lean loadings.
Primary Amine	An alkanolamine that has only one organic arm on the Nitrogen atom, thus nitrogen has 2 Hydrogen atoms attached to it. Examples are MEA and DGA®.
propionate	Propionate ion, one of the HSS anions; a WAA; determined by IC.
Residue, definition 0	Residue0 (wt%) = 100% – free amine wt% – water wt%. Residue0 intends to include all contaminants <u>including acid gas and (wanted) Bound Amine associated with acid gas</u> . Thus Residue0 can raise unneeded concerns. It is a small number from subtraction of large numbers, thus can have a high relative error, so is of little practical use.
Residue, definition 1	Residue1 (wt%) = 100% – Total Amine wt% – water wt%. Residue1 intends to include all contaminants <u>including acid gas</u> . It is a small number from subtraction of large numbers, thus can have a high relative error, so it is thus of little practical use until contaminants exceed about 5 wt%.

Table B-1. Analytical Definitions and Measurement comments	
<u>Term</u>	<u>Definition</u>
Residue, definition 2	Residue2 (wt%) = 100% – total amine wt% – water wt% – Acid Gas wt%. Residue2 should include all contaminants other than acid gas. It is a small number from subtraction of large numbers, thus can have a high relative error, so it is thus of little practical use until contaminants exceed about 3 wt%. Then, it is a signal to analyze for HSS, ADP, and NDP.
RFB	(see FA [Free Amine])
Rich Loading (RL)	Rich loading is the amount of acid gases (CO ₂ +H ₂ S) in the rich amine exiting the Absorber. This indicates the effectiveness of the Absorber. (see also LL)
RL	Rich Loading, the AGL in an amine solution exiting the absorber
S ₂ O ₃ ²⁻	Thiosulfate ion, one of the HSS anions; a SAA; determined by IC or sometimes by total oxidizable sulfides titration (caution: positive H ₂ S interference). In high concentrations only partially determined by the Total HSS method.
S ₂ O ₄ ²⁻	Sulfate ion, one of the HSS anions; a SAA; determined by IC.
SAA	Strong Acid Anions, a subset of HSS anions, which do not titrate with acid in aqueous solution. Determined by IC as polarizable ions. Determined by conductometric titration in the Total HSS method.
SAA	Strong Acid Anions, intending to mean all HSS anions, from the idea that all HSS anions are anions of acids that are stronger acids than the AG. In fact, acids as weak or weaker than AG could form HSS if they are less volatile and/or more soluble.
SCN ⁻	Thiocyanate ion, one of the HSS anions; a SAA; determined by AgNO ₃ titration or by IC.
Secondary Amine	An alkanolamine that has two organic arms on the Nitrogen atom, thus nitrogen has 1 Hydrogen atoms attached to it. Examples are DEA, DIPA, MMEA
SO ₃ ²⁻	Sulfite ion, one of the HSS anions; a SAA; determined by IC.
Solvent Factor	The molecular weight of the amine divided by 10. The solvent factor multiplied by the concentration in meq/g yields the concentration in wt%. In case of blends of more than one amine, the weighted average molecular weight of the blend is defined by the amine supplier, who determines it by formulation or by analysis of the solvent components. Because blends are proprietary, generally only the amine supplier is permitted to determine the average molecular weight by chemical analysis. The solvent factor may be discernable from a report that has Strong Cations expressed both at cation ppm and IHSS wt% as amine.
Strong Cations	Alkali cations which accumulate in the amine solutions from cooling water leaks or deliberate caustic addition. Measured as group by acid titration after preparation of sample through strong base anion exchange. Normally expressed as ppm Na or K whichever one is more prevalent. Also measure by Ion Chromatography (IC) or atomic emission (ICP) or atomic absorption (AA)

Table B-1. Analytical Definitions and Measurement comments	
<u>Term</u>	<u>Definition</u>
TA	Total Amine – Total concentration of amine in the circulating system. It can be measured by titration. It also is the sum of bound amine and free amine. The difficulty with titration method it measures all amine bases and the basic degradation products (See total bases). It is reported in MPR Customer Reports as the TA = total amine (obs) from titration – Amino Acids – degradation products like THEED.
TAB	Total Amine Bases = In MPR reports it is the TAB = total amine titration – Amino Acids. Depending on how and who is reporting it may be the same as the total base (TB) number or actual total bases (ATB)
Tertiary Amine	An alkanolamine that has three organic arms on the Nitrogen atom, thus nitrogen has no hydrogen atoms attached to it. Examples are MDEA and TEA. Tertiary amines cannot form amides or Oxazolidones (both NDP).
THEED	tris(hydroxethyl)ethylenediamine, a BDP of DEA
Total Bases (TB)	This can be total amine titration with out any adjustments. Actual total base (ATB) can be the same measurement = regenerable free base (RFB) + base bound to other acids
Total Nitrogen (TN)	Often used as an indirect measure of total amines. This can be done by CHN analyzers, or Total Nitrogen = Total Kjeldahl Nitrogen + Nitrate + Nitrite. Total nitrogen does not directly measure total amine. Amine degradation products may have nitrogen that can <u>not</u> absorb acid gases.
TPH	Total Petroleum Hydrocarbons. Can be measured by IR, gravimetrically, or GC. These methods all have strengths and weakness depending on the method, standards used, and the hydrocarbon species present. Normally reported as ppm.
TSS	Total Suspended Solids. Normally a gravimetric measurement (milligrams/liter) that roughly corresponds to ppm of solids in amine. It will not measure particles smaller than the filter pore size. Getting a good representative sample from the field is important. Particles may preferentially form on the rich side when H ₂ S or CO ₂ hits HSS or amino acids holding dissolved iron in the lean amine solution.
Viscosity	Several methods can be used. Normally reported as centiPoise. Normally an increase in contaminants and decrease in water content will give increased viscosity. If the viscosity is too high the gas treating becomes more difficult and also increased viscosity makes filtering and processing more difficult.
WAA	Weak Acid Anions, a subset of HSS anions, which do titrate with acid in aqueous solution forming an acid molecule. Determined by IC as weak acid ions. Determined by conductometric titration in the Total HSS method.
Water	Measured by Karl Fischer water titration. Other methods lack accuracy. Water concentrations are high, so sample size is very small. Extreme care is required to accurately measure the sample amount actually introduced into the titration. Expressed as wt%.