Chemical analysis in amine system operations

The array of contaminants that can disrupt the operation of alkanolamine systems needs to be precisely characterised and analysed

SCOTT WAITE, ARTHUR CUMMINGS and GLEN SMITH
MPR Services

Chemical analysis opens the door to understanding, responding to and preventing alkanolamine (amine) system operational difficulties. Unfortunately, the link between the analysis report and the amine system operation is often unclear. The uncertainty results from several factors that can lead to misunderstandings, misinterpretations, frustrations and mistrust of the lab. This article attempts to provide clear definitions of analytical terms, link them to their operational importance, translate terminology from different sources to a uniform set of terms, and expose analytical methods that can mislead you. This article also provides questions you can ask your chemist, lab analyst or amine vendor to avoid operational pitfalls and get the information you need from the analysis reports.

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_2S & CO_2) in the solution exiting the absorber
	Lean loading (LL)	Acid gas(H_2S & CO_2) in the solution exiting the regenerator
Water	Water	The remainder of the solution (if no contaminants)

Table 1

An alkanolamine acid gas scrubbing system is a 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 can continuously circulate. The simple acid base chemistry of the process can be monitored by a few analytical titrations (see Table 1), and operators need only to monitor temperatures, pressures and flow rates to balance the amine absorbing capacity with the acid gas removal requirement of the incoming petroleum gas or liquid. (The acid gas content of the sweetened product is, of course, the ultimate control measure, but is beyond the scope of this article.) This simplified view of amine systems and operational conditions is the basis on which the most common analytical methods were developed.

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 equipment longevity as well as 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, and yet the operator continues to rely on these few simple tests for day-to-day operations.

Increased awareness of the effects of contaminants on operations has led to an increased understanding of the variety and identity of contaminants that exist in amine systems. Common analytical methods have been adapted,

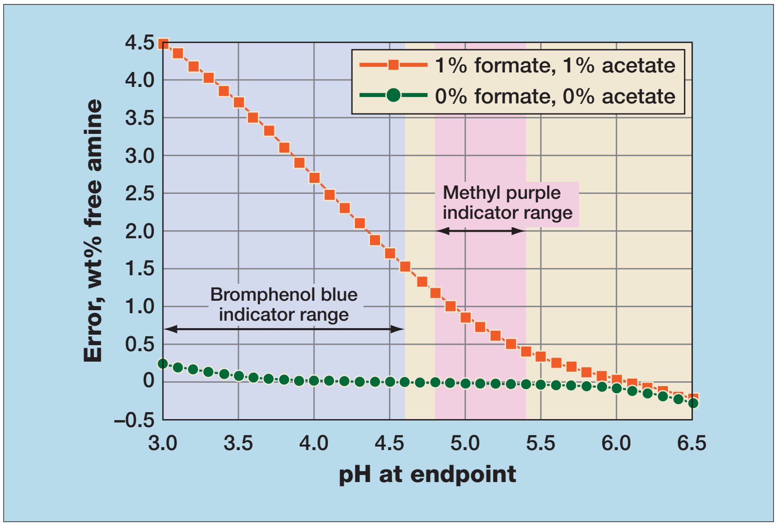

Figure 1 Endpoint pH affects accuracy of free amine titration

modified and sometimes misapplied to contaminant analysis. 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 that can be ambiguous, confusing and even misleading.

Better analytical methods needed

A prime example of misleading results is illustrated in Figure 1 and Table 2. When weak acids (such as formic acid, acetic acid, and so on) 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 colour indicator that provides accurate amine strength in a clean amine solution can grossly overestimate the amine strength of a solution that contains weak acid anions (HSS or LL). Note, for example, in Figure 1, that Methyl purple and Bromothymol blue are both acceptable indicators for the 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.

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	0.5	42.9	44.6	46.6	47.1
1	0	0.5	45.0	46.9	47.6	47.7

Table 2

Understanding analyses

With knowledge of the preceding information, the engineer responsible for the amine system can now ask the analytical chemist or operator, "What endpoint indicator do you use for the amine strength titration?" If the chemist responds "Bromophenol blue" or "pH 4.5", the engineer knows that amine strength results are probably higher than their actual level, unless there are no weak acids in the amine solution.

The better titration methods require the tracking of pH or conductivity during the titration and determination of 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.[1,2]

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

Amine system is supposed to make salts

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

Alkanolamines are bases.

Regenerable salts from acids gases in amine solutions

Acid + vase → cation + anion

Acid	Base	Salt	Salt name
H_2S	Free amine ("Am")	$AmH^+ + HS^-$	Aminium bisulphide
$CO_2 + H_2O \rightarrow H_2CO_3$	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 3

Bases react with acids to make salts. Acid gases are absorbed and held in amine solutions because the amine forms a salt with the acid gas. The acid gas becomes an anion (negatively charged ion) and is associated with an amine cation (positively charged ion). The acid gas ion is no longer in a gaseous state and it cannot leave the amine solution as long as it remains as an anion.

The regenerable salts in Table 3 and the HSS in Table 4 are written to emphasis the separateness of the ions. A cation is a positively charged molecule that is physically disconnected from its neighbouring 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 they are continually changing partners. This view of ions is critical to the understanding of amine acid gas absorption and regeneration.

For example, H_2S absorbed in an amine solution is not bound to the amine. Rather, the amine has taken a hydrogen ion (H^+) from the H_2S, creating an AmH^+ cation and 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 H_2S, which has low solubility and high volatility and will exit the solution, unless another amine molecule reacts with it and removes one of its H^+ to form another salt.

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 and lower pressures AmH^+ more readily releases its H^+, and the anions of the acid gases readily take the H^+, creating gases that are less soluble and more volatile at the elevated temperature and decreased pressure of the regenerator.

HSS, 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 they do not as readily accept the H^+ offered by the AmH^+), and are more soluble and less volatile than the acid gases (thus they do not 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 HSS: salts whose cation is a strong cation such as sodium or potassium. These are often called inorganic HSS (IHSS) and are formed in amine solutions from the addition of caustics (sodium or potassium hydroxide or carbonate). The last two entries illustrate that an excessive concentration of strong

HSS from acids in amine solutions

Acid + base → cation + anion

Acid	Base	Salt	Salt name
Formic	Am	AmH^+ + formate$^-$	Aminium formate
Acetic	Am	AmH^+ + acetate$^-$	Aminium acetate
Propionic	Am	AmH^+ + propionate$^-$	Aminium propionate
Thiocyanic	Am	$AmH^+ + SCN^-$	Aminium thiocyanate
Thiosulphuric	Am + Am	$AmH^+ + S_2O_3^= + AmH^+$	Aminium thiosulphate
Hydrochloric (HCl)	Am	$AmH^+ + Cl^-$	Aminium chloride
Sulphuric	Am + Am	$AmH^+ + SO_4^= + AmH^+$	Aminium sulphate
Formic	NaOH	Na^+ + formate$^-$	Sodium formate
Acetate	NaOH	Na^+ + acetate$^-$	Sodium acetate
Acid gases are heat stable with caustics; for example:			
H_2S	NaOH	$Na^+ + HS^- + H_2O$	Sodium bisulphide
HCO_3^-	KOH	$K^+ + CO_3^= + H_2O$	Potassium carbonate

Table 4

Solvent parameters of amine solutions

Parameter	Analyte	Description and role
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 a 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.

Table 5

cations makes HSS of the anions of acid gases, causing the lean loading of the regenerated amine to rise. Strong cations must never be allowed to rise to the level that any acid gas becomes heat stable. This starts to occur when the molar ratio of strong cations to HSS anions reaches approximately 0.66.

Acid gas regeneration is aided by a low concentration of amine HSS, because they increase the population of AmH^+ by decreasing the pH. The anions of acid gases then have a higher probability of obtaining H^+ to convert back to the gaseous state and escape the solution of amine.

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.

HSS reduce amine strength, increase corrosivity, increase viscosity, increase density and displace water from the amine solution.[3,4] All these have deleterious effects on amine system operations. It is thus very important to know what and how much salt is accumulating in your amine system.

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. If there are no contaminants in the amine system, the Table 1 analyses would be sufficient — water could even be determined by difference. However, contaminants are common in amines systems and a more detailed analysis is required. Table 5 shows several parameters requiring analysis for the proper operation of clean amine systems.

The trends in the amine system should be monitored on a regular basis. When BA rises or TA plus water departs significantly from near 100%, the amine system could be becoming contaminated and more information is needed. The second-tier analyses — for dissolved substances — are listed in Table 6.

The numerous analytes listed in Table 6 can be daunting. The several analytes may each show a different result, or overlap, or even disagree with one another, requiring informed interpretation of the respective results.

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

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

Reconciling various analytical methods

When you compare 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 HSS content of this sample" could have the following correct answers:

HSS anions	14 609 ppm(m)
Total HSS	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 sometimes 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 HSS: the anions and the amine equivalent cations. The others have good utility, however, and need to be understood.

As can be seen in Table 8, there are a large number of parameters that are measured

Dissolved substances in amine solutions (other than solvent amine)

Type	Analytes	Description and role
Acid gas (AG)	Rich loading (RL)	Acid gas (H_2S & CO_2) in the solution exiting the absorber
	Lean loading (LL)	Acid gas (H_2S & CO_2) in the solution exiting the regenerator
	H_2S, CO_2, acid gas loading (AGL)	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)	HSS; total HSS; BA; HSAS; IHSS; individual anions*; ATB-RFB; conductivity	Acids that 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)
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), eg, K+, Na+; corrosion metal ions (Fe, Cr, Ni, etc) inorganic HSS (IHSS)	Alkali cations that 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, thiosulphate, sulphate and sulphite .

Table 6

Insoluble, partially soluble or dispersed substances in amine solutions

Type	**Analytes**	**Description and role**
Solids	Total suspended solids (TSS)	From corrosion products, chemical and physical; TSS contribute to further corrosion, flow restrictions, and plugging. TSS stabilise 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

Table 7

by a variety of techniques, and a thorough understanding of the terminology is required to correctly interpret amine analysis reports and to take action based on the analysis.

Questions to ensure measurements are clear and understood

Proper sampling is essential to achieving good analysis results, and understanding how the sample was taken is essential in helping you interpret the results. The following questions should be suitably answered before the analyst or operator takes a sample:

- Was the dead leg flushed before taking the sampling?
- Were the operating conditions of the unit recorded when the samples were taken? Is there a plant upset or unique operating conditions?
- Was the reason for sample collection recorded (routine or non-routine troubleshooting)?
- Where was the sample taken? Upstream or downstream of the filters and carbon beds?

You should make sure that the measurements for free amine (FA) or amine strength are correct so you know how much amine is available for acid gas adsorption. The following questions are helpful to interpret the results:

- Is it a titration with acid? If yes, good.
- Is the endpoint of the titration determined by inflection points in a conductivity or pH curve? If yes, good
- Is the endpoint determined by colour indicator? If yes, worry about accuracy
- Is the endpoint determined by "dead-stop" at a specified pH? If yes, worry about accuracy
- Spiking with acetic acid before titration can help get a more accurate endpoint for FA.

An important parameter for operational control is the total concentration of the amine in the unit. The questions below should be asked so you can understand how the total level of amine was determined:

- How is the total amine test done (GC, IC, HPLC, titration or other)?
- If GC, IC or HPLC, what amines are quantified and are there noteworthy not quantified/unidentified peaks?
- If titration, are other basic species such as 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.

One of the most important analyses in amine systems is the measurement of HSS. A number of methods can be used for this analysis, and it is recommended that more than one method be used and the results compared to make sure accurate results are obtained. These questions are useful in obtaining a good understanding of the results:

- How is the HSS measurement made (IC or titration)?
- If by IC, the individual analysis of species should be available. See if the common anions are analysed for formate, acetate, propionate, glycolate, oxalate, chloride, thiocyanate, thiosulphate, sulphate and nitrate
- If by titration:
  - Is a direct titration of the amine sample with base? If so, the result is BA.
  - How is lean loading (AGL) removed? If via boiling of a direct sample, worry about false high results
  - How are strong cations removed before analysis or how is their effect 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.

Strong cations can enter amine systems unintentionally through heat exchanger leaks, from the treated product or intentionally by the addition of caustic to neutralise HSS. Proper analysis is important to make sure they do not contribute to high lean loading and stripping difficulties or contribute to viscosity and corrosion problems. There are several methods of analysis for strong cations, and the following questions should be asked:

- How are strong cations (sodium, potassium and calcium, for instance) determined?
- If by IC or ICP:
  - Was the signal within the calibration range?
  - Are there any false highs due to interferences (such as amine with K^+ in IC)
- If by titration:
  - Was a sufficient strong-base anion exchange resin used to absorb all the LL and HSS anions (at least two times the equivalent)?
  - 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)

- Only strong alkali and alkaline earth metals are detected by titration.

It is important to measure metals in order to have an early detection system for possible operational difficulties due to corrosion products or loss of metal integrity in the unit. Metals are measured by ICP and AA, and there are several relevant questions you should ask and items you should consider:

- Was the sample filtered or digested? (Dissolved or total metals?) High dissolved metals in lean amine samples indicate the presence of HSS, amino acids and/or polymeric amines (BDP)
- 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, the measurement is of only the dissolved metals
- If the samples are not filtered until after acid digestion, the metals in the solids (total metals) are included in the metals report
- Generally, it is more instructive to determine the metals in the filtered solids separately from the liquid, so solids and dissolved solids profiles can be determined.

Performing a mass balance or "residue calculation" can be instructive. It requires an accurate water analysis by Karl Fisher titration, an accurate total amine measurement, an accurate knowledge of the amine molecular weight (which may be difficult if it is a blended or formulated amine), and an accurate analysis of strong cations, HSS, amino acids, AGL, BDP, NDP and amides. A mass balance of less than 100% can indicate that there are contaminants present that have not been analysed. A mass balance of greater or less than 100% can also indicate errors in the analysis methods, especially for total amine and water.

If your lab does not have the capability of running all the tests, do not hesitate to use an outside lab to complement your in-house testing. It is also a good idea to have a complete analysis done by an outside lab once a year to check your in-house analysis results. If contaminants are growing or changing, you may be advised to have outside analysis done on a more frequent basis. Remember that HSS, amino acids and BDP contribute to corrosion and can cause severe damage to the amine treating unit.

Analytical symptoms of some amine system problems

Symptom	Possible Interpretations
FA decreasing	- 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 CO_2 service
Total HSS increasing	- HSS ingress - Water content decreasing - Corrosivity increasing - Need HSS removed
FA increasing while BA increasing	- FA analysis error: FA report includes weak acid HSS
LL rise with no change in operating conditions	- Greater AG load in absorbers - Strong cations ingress into solvent
Total HSS > BA	- Caustic ingress or addition - Cooling water leak into amine solution
BA > total HSS	- Amino acids present (not included in total HSS) - BA includes high LL
Thiosulphate HSS	- Oxygen ingress - SO_2 breakthrough (Claus tail gas)
Bicine (and other amino acids)	- Oxygen ingress (gas plants) - O_2, SO_2 and/or S_2O_3= attack (refinery)
Strong cations	- Caustic addition - "Amine slops" added to amine and included some caustic - Cooling water leak into amine - "Hidden" HSS - Foaming tendency increasing (soaps)
Formate HSS	- 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 (do not throw it away)
Acetate HSS	- Acetonitrile ingress - Oxygen ingress
Thiocyanate (SCN^-) HSS	- Cyanide reacting with H_2S
Chloride HSS	- Cooling water leak - HCl ingress
Solids (TSS) rising	- Corrosion - Filters inadequate or spent
TPH	- Hydrocarbon carryover into amine: inadequate knock-out drum
"Residue" increasing, but BA not	- Caustic ingress or addition - Cooling water leak into amine solution - Amine chemical degradation

Table 9

What information is revealed by analysis of contaminants?

By closely monitoring trends in the analytical data, you can detect possible operational problems before they become a big problem for the unit. Table 9 provides some examples.

Summary

We have discussed 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 can lead to confusion if the analytical reports are not properly understood and interpreted. 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 for amine analysis 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), H_2S and CO_2, total HSS, including WAA and SAA estimates from conductivity titrations, strong cations (SC), chloride, thiocyanate, amino acids, amides and water. With the exception of CO_2, these can all be done with an autotitrator.

A mass balance or residue calculation using the analysis in the previous paragraph yields an estimate of basic degradation products (BDP) and neutral degradation products (NDP).

Instrumental methods can be added to measure total nitrogen (TN), amine species by GC or IC, and HSS speciation by IC. Then, by "amine balance" and "nitrogen balance", BDP and NDP estimates might be segregated. These can be supported by HPLC and GC identification of specific BDP and NDP species.

Other important measurements that can provide information on the health of the amine include total suspended solids (TSS), total petroleum hydrocarbons (TPH), foaming tendency, foam break time, density, pH, conductivity, viscosity and surface tension.

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

A plant needs to have locally only an automatic titrator, conductivity meter and probe, pH meter and probe, sulphide ion-selective electrode and reference electrode, CO_2 analyser, and Karl Fischer titrator in order to provide the most important analyses (free amine, total amine, bound amine, H_2S, CO_2, total HSS, strong cations, chloride, thiocyanate and water). The other analytes can be done monthly, quarterly or as needed by your company's central analytical lab, amine vendor or reclaimer.

A further table (Table 8) providing comprehensive reconciliation of analytical methods and their reports is included in the web version of this article. Go to www.eptq.com

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Scott Waite is Vice President of Technology with MPR Services, Inc., Dickinson, Texas. He has managed the R&D process to develop new and improved methods for amine and glycol reclamation, and treatment of produced and flow backwater. He is currently an Adjunct Professor of Chemistry at University of Nevada, Reno, and holds a BS in chemistry from the University of Arizona and a PhD in physical/analytical chemistry from the University of Utah.

Arthur Cummings retired from MPR Services in July 2012. During his 21 years as Vice President of Technology, MPR helped hundreds of refineries, gas plants, ammonia plants, syngas plants, chemical plants and steel mills improve the operation of their amine units. He holds a PhD in analytical-physical chemistry from Brigham Young University.

Glen Smith is Technical Manager with MPR Services. He managed MPR's laboratory from 2005 through 2012, and helped develop and improve methods of analysis for amines and glycols. He holds a PhD in inorganic chemistry from Purdue University.

Reconciliation of analytical methods and their reports

Reported as	Really is	Method description	Comments
Free amine (FA) or regenerable free base (RFB)	Free amine (including basic degradation products (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 conductivity to calculate correct endpoints pH or 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	
Nitrogen balance	Neutral degradation products (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, itemised (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 derivatisation to avoid errors from on column degradation
nFDEA, FDEA, DEAF, FDIPA DIPAF, FMEA, etc	Amides, formylamines (part of NDP)	HPLC or GC (with derivatisation)	(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_2S 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
H_2S or acid gas loading (AGL)	H_2S	Titration of sulphide by $AgNO_3$; direct titration of amine sample diluted in water	Most reliable H_2S method; can detect mercaptans separately; does not detect CO_2 so may not be total AGL
H_2S or AGL	$H_2S + S_2O_3^= + SO_3^=$	Titration of excess Iodine with sodium thiosulphate after addition of amine sample to acidic Iodine	False high H_2S results if thiosulphate HSS are present
Acid gas loading (AGL)	$H_2S + CO_2$	Sum of direct measure of H_2S and CO_2 individually. Best if H_2S 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	$(H_2S + CO_2)$/FA, mol/mol	Most common expression of LL and RL

Reported as	Really is	Method description	Comments
Acid gas loading (AGL)	AGL/TA	$(H_2S + CO_2)$/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	Poor 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 or by IR spectroscopy; removes H_2S before titration for the titration method.	The only reliably accurate methods for CO_2 in all amine solutions
HSS, total HSS, or HSS by titration acids	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 thiosulphate is under-reported. Can determine weak and strong acids as separate groups if use conductivity (see Attachment A). 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 SC.	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 Purging of AG by boiling could lose formate HSS: use N_2 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 do not
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
Strong acid anions (SAA)	HSS species, anions of strong acids only (SAA)	Sum of the strong or "polarisable" anions determined individually by ion chromatography	Include chloride, thiocyanate, sulphate, thiosulphate, nitrate, oxalate, sulphite, bromide, phosphate, arsenate (anions of stronger acids than formic acid)
Strong acid anions (SAA) (SAA)	Anions of strong acids	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
HSAS or BA	BA	BA corrected = BA observed minus extra HCO_3^- contribution, calculated by charge balance: LL + HSS-strong cations.	Actual AmH^+ in solution as received. Can be used in mass balance where amino acids are itemised separately. Estimate HCO_3^- correction from TIC, pH, and K_{a2}
HSAS accuracy	HSAS	Total HSS – IHSS or total HSS – strong cations	Generally reliable; accuracy depends on total HSS
HSAS	HSAS	HSS species – IHSS or HSS species – strong cations	May underestimate (see HSS species)
HSS neutralised	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%)
$S_2O_3^=$ HSS	$S_2O_3^= + SO_3^= + H_2S$	Titration of excess Iodine with sodium thiosulphate after addition of amine sample to acidic iodine	False high thiosulphate if H_2S is present

Reported as	Really is	Method description	Comments
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 $S_2O_3^=$	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. (eg, sea or ground water contamination)
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_2O, leaving all strong cations with an OH^- companion anion. The OH^- is then titrated with acid, equalling the strong cations	Excellent accurate determination of the strong cation characteristic in amine solutions,
Na^+, K^+, Ca^{2+}, Mg^{2+} K^+	Strong cations	ICP or IC measurement	ICP accurate; IC may have interference from amines for
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: sulphated ash, carbonate ash, oxide ash	Typically interpreted as Na ash, but includes all metal cations present. Na ≈ sulphated ash/3.1, carbonate ash/2.3, Na_2O/1.4
IHSS (inorganic heat stable salts)	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, amino acid standardisation applied to peaks with retention similar to the known amino acid standards – this is an estimate of amino acid level.	Good approximation; check against total amino acids by charge balance
Amino acids, total	Total amino acids by charge balance	Amino acids = BA observed – total HSS – AGL - HCO_3^- + strong cations	Fair 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.