

**AN ANALYTICAL METHOD  
FOR DETERMINING  
BOUND AND FREE ALKANOLAMINES  
IN HEAT STABLE SALT CONTAMINATED SOLUTIONS**

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## ABSTRACT

A conductometric titration method has been developed to determine the true available alkanolamine in solutions used for H<sub>2</sub>S and CO<sub>2</sub> removal from refinery gas. In the presence of heat stable salts and sodium contamination, traditional indicator based titration methods were found to be inaccurate by including weak acid anions as available amine. The new method will help operators to correctly monitor alkanolamine systems and to take corrective action for optimization.

## INTRODUCTION

Aqueous amine solutions are used at refineries and well sites to scrub acid gases from gas streams. The trapping of the acid gas in the solution involves an acid-base reaction between the acid gas and the amine, which results in a protonated amine and a deprotonated anion of the acid gas. Once protonated, or "bound", an amine molecule is no longer available ("free") to trap another molecule of acid gas. Eventually, the scrubbing efficiency of the amine solution decreases to unacceptable level and/or the corrosivity of the solution becomes intolerable. A method of directly measuring bound and free amine concentrations could be helpful for process control.

Regeneration of used amine for reuse is economically and environmentally desirable. Some acids can be stripped from amine solutions by heat, freeing some of the bound amine and reducing the corrosivity. Sodium hydroxide frees bound amine, renewing the acid scrubbing capacity, but not reducing the concentration of anions from acids absorbed by the solution. Regeneration methods could be more efficiently and beneficially conducted if a method of directly measuring bound and free amine concentrations were available.

Analytical methods are available for determining total amine and total heat stable salts (HSS), but these do not address the issue of scrubbing typically performed by titration with strong acid. Bound amine, which can be a sensitive indicator of HSS build-up, is generally not directly determined, but is calculated from the difference of two much larger quantities, total and free amine, and may not be accurate.

Titration for free amine are often practiced in such a way that weak acid anions (such as acetate and formate) interfere, and an inflated free amine concentration is reported. Symptoms of this situation include amine concentrations reported at greater than 100% of the amount added to the system, or amine concentrations from analysis not dropping in accordance with rising corrosion rates. If contactor amine flow is set using an erroneous inflated free amine concentration, acid gas loading may be too high, product H<sub>2</sub>S will be too high, or system corrosion rates will increase. All these lead to reduction in profits.

This report describes a method by which free and bound amine are determined directly and separately. Total amine is calculated from the sum of the bound and free. Amine concentrations from 100 ppm to 95 wt% can be determined. Unique to this method is the segregation of free amine from weak acid anions and the determination of excess NaOH.

The method employs common titration equipment, but uses conductance, rather than pH, for endpoint detection. Conductance measurement is more rugged than pH, often provides sharper endpoints, and reveals much about the chemistry of the amine solution. The method could be used

to determine the amine concentration in sour gas scrubbing solutions, to monitor the amine activity in refinery operations, to detect amine in aqueous waste, or to follow amine regeneration processes.

## EXPERIMENTAL

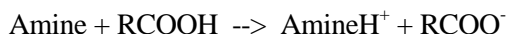
Procedural details of the conductometric titration are provided in the Appendix. Amine samples were obtained from refinery operations which use about 45 wt% methyldiethanolamine (MDEA). Measurement of pH was accomplished with a glass electrode and the potentiometer of an automatic titrator, referenced against pH 4 and pH 7 buffers.

## AMINE REACTIONS

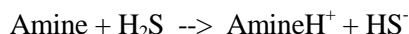
Amine solutions trap acid gases with the aid of a chemical reaction in which the nonvolatile amine "salt" is formed. In the solution, the salt primarily exists as dissociated cation and anion:



For example,



or,

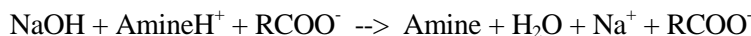


If heating the solution reverses the reaction to a significant degree, the amine salt is a "heat labile salt", as are those formed from hydrogen sulfide and carbon dioxide. For example, in a steam stripper,



The other salts are called "heat stable salts" (HSS). These pass through the steam stripper with the rest of the amine. Typical HSS include acetate, formate, sulfate, thiocyanate, and thiosulfate salts.

Addition of NaOH frees the bound amine, but the anions remain in the solution as sodium salts, all of which are heat stable:



The heat stable salts accumulate with time in a circulating amine system. The amine salts represent a reduction in scrubbing capacity. The amine salts and the sodium salts both increase the ionic content of the solution, which affects hydrodynamics and corrosivity and, in extreme cases, leads to precipitation of solids from the solution.

## DETERMINATION OF AMINES BY TITRATION

Amines react quantitatively with acids according to the first reaction shown above. It follows that if one measures the amount of acid used to consume all the amine in a measured amount of solution, one can calculate the concentration of the free amine in the solution. Similarly, if one titrates a solution with a base, e.g., NaOH, according to the last reaction shown above, one can calculate the concentration of bound amine in the solution.

In such titrations, the accuracy of the calculated result depends on the accuracy with which one can mark the equivalence point of the titration. The equivalence point is that point during the titration when the amount of acid (or base) added is exactly equivalent to the amount of free (or bound) amine in the solution. The operators estimate of the equivalence point is called the endpoint of the titration. The endpoint is generally determined from a change in some property of the solution, such as pH, color, conductance, etc.

Figure 1 illustrates the error potential when titrating lean amine solutions to a fixed pH, as determined by pH meter reading or color indicator. The vertical axis marks the error in wt% amine for endpoint pH magnitudes shown on the horizontal axis. The pH ranges of two common color indicators are shown by shading. For illustration, an amine solution containing 45 wt% MDEA is assumed. When the amine is fresh (plus signs in Figure 1), the pH falls so rapidly through the equivalence point region that an endpoint taken anywhere within the illustrated range would result in insignificant error. In contrast, a lean amine solution containing weak acid anions, e.g., 1 wt% acetate and 1 wt% formate (squares in Figure 1), does not change pH rapidly after the free amine equivalence point. In fact, the equivalence point is shifted to higher pH. The weak acid anions also consume added hydrogen ions:



The choice of endpoint pH will greatly affect the accuracy of the determination of free amine. In this example, a fixed pH of 4.5 would yield a positive 1.7 wt% error, whereas the pale yellow of bromphenol blue might be perceived at 3.5 to 3.2 pH, resulting in a positive error of from 3.7 to 4.2 wt% MDEA. The magnitude of the error will thus depend on technician, technique, and indicator, as well as the weak acid anion concentration. The error can be large enough to "find" nearly 100% of the total amine to be free amine, even though heat stable salts are present. If the amine has been treated with NaOH, greater than 100% of the amine can be "found" by fixed pH endpoint titration (see Table 1).

Potentiometric monitoring of the acid titration of an amine, acetate and formate solution, using a glass electrode, revealed two equivalence points ("pH" curve, Figure 2). The first, the amine equivalence point, was clearly defined at about 6.4 pH. The second, for the weak acid anions, was not well defined, but could be estimated at about 3.4 pH.

Conductometric monitoring of such a titration, in contrast, provides clearly defined endpoints at both equivalence points ("conductance" curve, Figure 2). In addition, the trained operator can tell from the slope of the conductance trace what is being titrated, whether free amine, weak acid anions, or excess OH<sup>-</sup>.

## CONDUCTOMETRIC TITRATIONS

Four determinations characterizing amine solutions can be made by conductometric titration. Titration with acid (HCl) can determine excess OH<sup>-</sup>, free amine, and weak acid anions. Titration with base (NaOH) determines bound amine.

Excess  $\text{OH}^-$  might be present if NaOH were added to an amine system in an amount which exceeded the equivalent amount of amine heat stable salts, such as in the last entry of Table 1. The excess  $\text{OH}^-$  is first to react with acid added during titration. After the  $\text{OH}^-$  is consumed, the acid titrant reacts with free amine, then with any weak acid anions. The conductometric recording of the titration (Figure 3) clearly shows the separate reactions with the 3 types of bases. Table 2 summarizes the reactions and conductance trend for each of the steps marked in Figure 3.

When the concentration of weak acid anions is small, step H3 may be difficult to discern. Step H3 may be extended by addition of a measured amount of standardized acetic acid solution (see Appendix).

Titration with base (NaOH) produces a characteristic conductance trace with nearly zero slope. The equivalence point is followed by a sharply rising slope, as illustrated in Figure 4 and explained in Table 3. Of course, an amine solution containing excess  $\text{OH}^-$  would show no bound amine.

## CONCLUSIONS

A method had been developed for determination of 4 key properties relating to the performance of alkanolamine (MDEA, MEA, DEA, etc.) solutions. These include concentrations of Bound Amine, Free Amine, weak acid anions and excess hydroxide. The method is an improvement over common titration methods because it clearly segregates these properties, avoiding errors which lead to inefficient operation of amine systems. The Bound Amine determination is a unique addition to amine analysis, providing a sensitive monitor of the consumption of amine scrubbing capacity.

<b>TABLE 1</b>						
<b>ERROR OF FIXED pH ENDPOINT TITRATION</b>						
<b>45 wt% MDEA</b>						
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	<b>45.0</b>	45.0	45.1	45.2
1	1	0	<b>40.3</b>	42.0	44.0	44.5
1	0	0	<b>43.0</b>	44.3	45.0	45.1
1	1	.5	<b>42.9</b>	44.6	46.6	47.1
1	0	.5	<b>45.0</b>	46.9	47.6	47.7

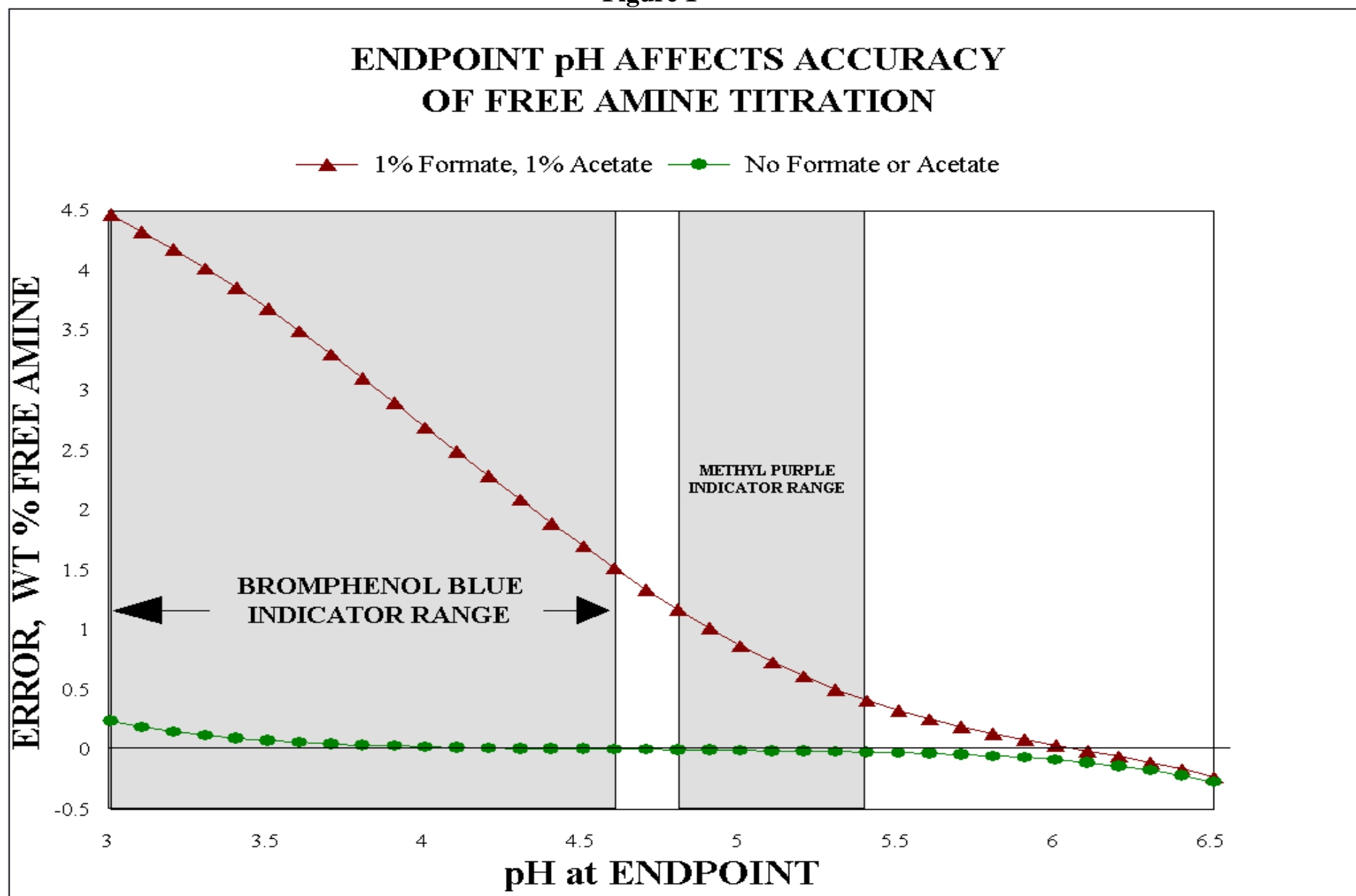
<b>TABLE 2</b>		
<b>CONDUCTOMETRIC TITRATION OF AMINE</b>		
<b>WITH HCl</b>		
STEP	REACTION	CONDUCTANCE SLOPE
H1	$\text{OH}^- + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{Cl}^-$	$\ll 0$
H2	$\text{Amine} + \text{HCl} \rightarrow \text{AmineH}^+ + \text{Cl}^-$	$> 0$
H3	$\text{RCOO}^- + \text{HCl} \rightarrow \text{RCOOH} + \text{Cl}^-$	$\sim 0$
H4	$\text{HCl} \rightarrow \text{H}^+ + \text{Cl}^-$	$\gg 0$

<b>TABLE 3</b>		
<b>CONDUCTOMETRIC TITRATION OF AMINE</b>		
<b>WITH NaOH</b>		
STEP	REACTION	CONDUCTANCE SLOPE
N1	$\text{AmineH}^+ + \text{NaOH} \rightarrow \text{Amine} + \text{H}_2\text{O} + \text{Na}^+$	$\sim 0$
N2	$\text{NaOH} \rightarrow \text{Na}^+ + \text{OH}^-$	$\gg 0$

## **LIST OF FIGURES**

1. Endpoint pH Affects Accuracy of Free Amine Titration
2. pH and Conductometric Titrations of MDEA and Acetate and Formate HSS.
3. Conductometric Titration of Free Amine, Excess OH<sup>-</sup>, and Weak Acid Anions
4. Conductometric Titration of Bound Amine with NaOH

Figure 1



# pH and CONDUCTOMETRIC TITRATIONS

MUREX with ACETATE and FORMATE IONS

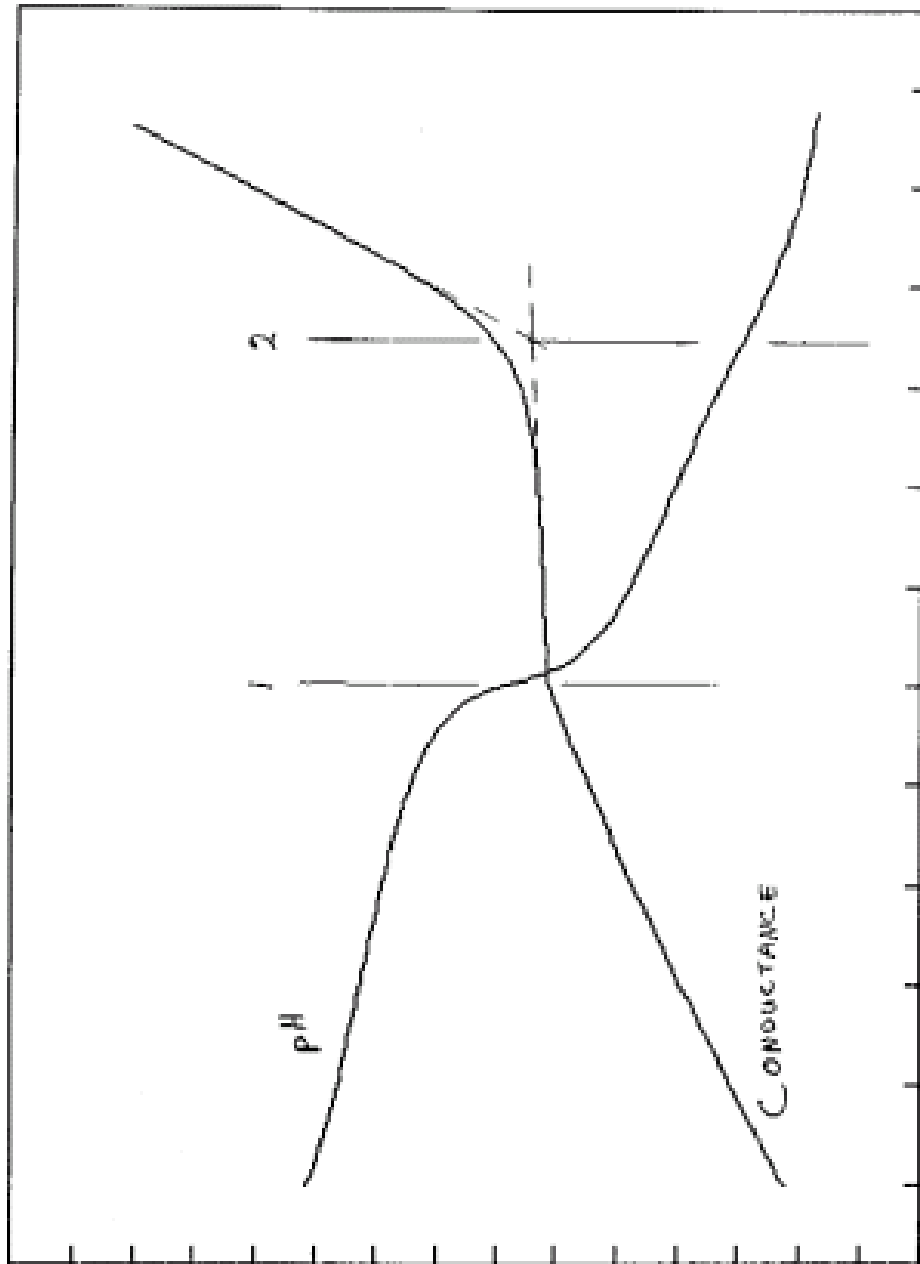


FIGURE 2

# CONDUCTOMETRIC TITRATION of FREE AMINE,

EXCESS  $\text{OH}^-$ , and WEAK ACID ANIONS

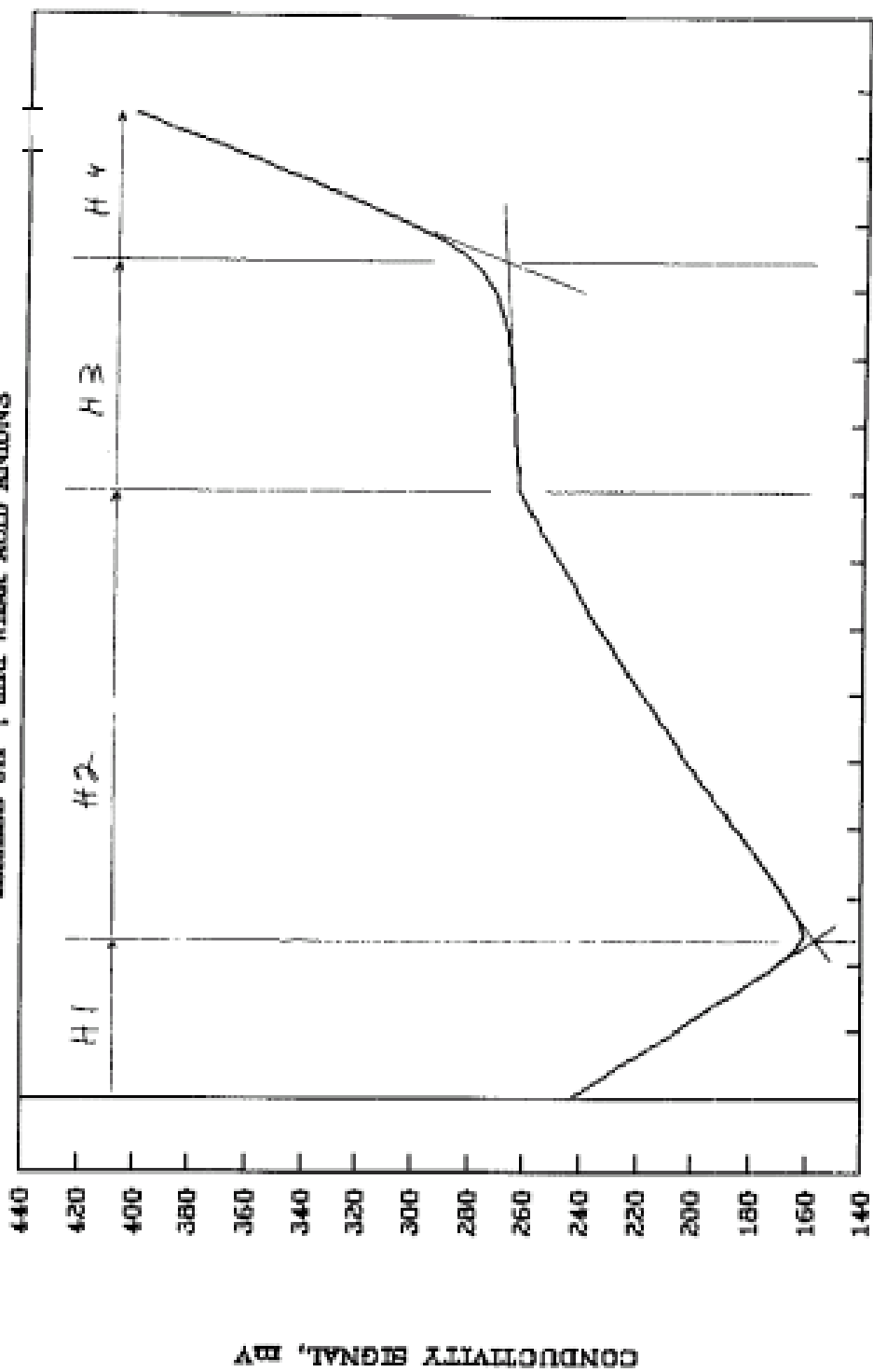
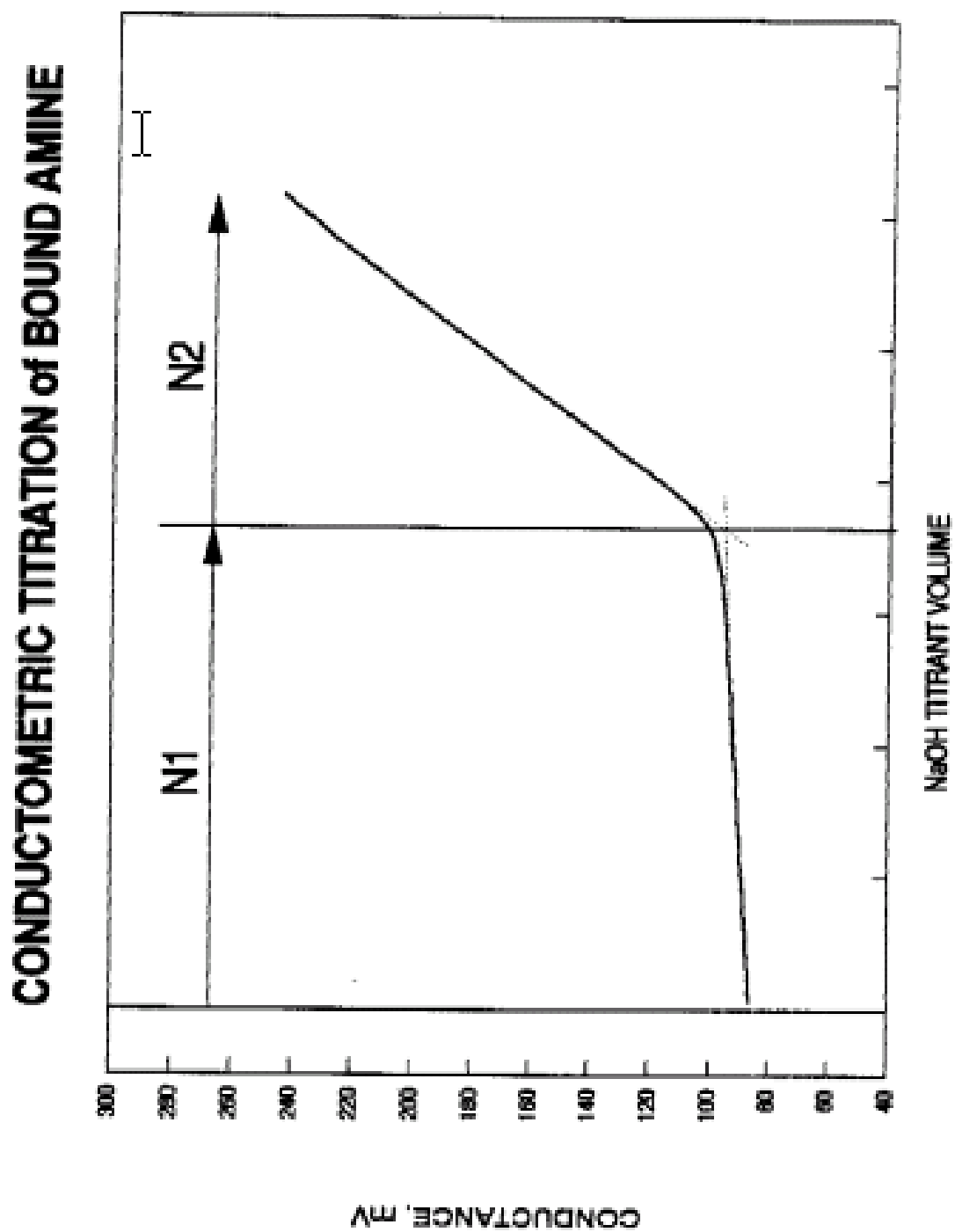


FIGURE 3

HCl TITRANT VOLUME

FIGURE 4



## APPENDIX

### PROCEDURE FOR THE DETERMINATION OF BOUND AND FREE AMINE BY CONDUCTOMETRIC TITRATION

#### SCOPE

Aqueous solutions of amines, such as monoethanolamine (MEA), methyl diethanolamine (MDEA), and diethanolamine (DEA), are analyzed to determine the concentrations of "bound amine" (protonated amine; amine which has neutralized an acid), "free amine" (amine which has not reacted with an acid), anions of weak acids (e.g., acetate, formate), and excess NaOH. Total amine concentration is calculated as the sum of bound and free amine concentrations. Amine concentrations from 100 ppm to 95 wt% can be determined.

#### KEY WORDS

MDEA, MEA, DEA, Lean Amine Reclamation, Heat-Stable Salts, Conductimetry, Titration

#### OUTLINE OF METHOD

A sample of amine solution is mixed with water and titrated with NaOH while monitoring the electrical conductance of the solution. From the consumption of NaOH the bound amine concentration is calculated. A similar titration with HCl leads to the calculation of free amine and weak acid anions concentrations. Addition of a known amount of acetic acid to the titration solution enhances the accuracy of free amine and weak acid anion determinations. Excess NaOH in the amine solution is determined by a third titration, when necessary.

#### APPARATUS & MATERIALS

- Conductance meter and probe (YSI Model 32 or equivalent); for automatic titration, meter should have -2 to +2 V analog output.
- Buret, 20 mL capacity, readable to 0.02 mL (manual volumetric, manual gravimetric, or Metrohm 665 Dosimat, or equivalent).
- Balance, analytical, readable to 0.0001 g.
- Beakers, 100 mL.
- Continuous stirring device (e.g., magnetic stirrer and 1/8 x 1 inch stirring bar).
- Titration recording and graphing device (paper and pen, or Metrohm 670 microprocessor-controlled automatic titrator, or equivalent).

## REAGENTS

1. NaOH solution, 0.1 N, aqueous (Fisher SO-S-276, or equivalent).
2. HCl solution, 0.1 N, aqueous (Fisher SO-A-54, or equivalent).
3. Acetic acid solution, 1 N, aqueous.
4. Water, conductance grade (less than 0.5 micromho conductance)
5. Potassium acid phthalate (potassium biphthalate), primary standard.

## SAMPLE PREPARATION

Portions of amine solutions are taken as received, weighed, and transferred to the titration beaker.

## AUTOMATIC TITRATOR PARAMETERS

Automatic titrators should be set to titrate until the specific conductance has increased at least 200 mmhos/cm (200 mmhos for cell constant of 1) from the starting conductance. A monotonic titration in increments of about 0.1 mL has worked well. Specific parameter settings will depend on the titrator model in use.

## QUALITY CONTROL

Reagents should be stored to prevent titer changes due to evaporation or contamination. HCl reagent and Acetic Acid reagent titers should be verified daily by one standardization titration. NaOH reagent titer need be verified only when the HCl titer goes beyond control limits. Statistical process control charts should be maintained on the titer checks. Restandardization is required when control limits are exceeded.

## REAGENT STANDARDIZATION

Reagents are standardized by titration with colorimetric, potentiometric, or conductometric finish. NaOH reagent is standardized against dried primary standard potassium acid phthalate. HCl and Acetic Acid reagents are standardized against standardized NaOH reagent. The standardized titer of the reagents must be the average of at least 3 determinations.

## PROCEDURE

Of the three titration procedures given here, the Bound Amine should be performed first. Only if no bound amine is detected, should the Excess OH<sup>-</sup> titration be done. The Free Amine procedure is affected by Excess OH<sup>-</sup> when present.

### A. Bound Amine

1. Weigh 2 grams (see Note 1) of amine solution and quantitatively transfer to the titration beaker. Record weight to the nearest 0.002 g.

2. Add conductance water (ca. 45 g) to bring solution level to top of vent holes in conductance probe. Begin continuous stirring without visible vortex.
3. Titrate with 0.1 N NaOH to at least 3 mL beyond the beginning of the increased slope evidencing excess OH<sup>-</sup> (see Figure A-1).
4. Determine the equivalence point from a graph of the titration curve (conductance vs. mL of titrant), and calculate the bound amine concentration (see "Calculations").

B. Free Amine

1. Weigh 0.3 grams (see Note 1) of amine solution and quantitatively transfer to the titration beaker. Record weight to the nearest 0.0005 g.
2. Add 0.4 grams (or 0.4 mL) Acetic Acid reagent (see Note 2) to the titration beaker. Record the amount to the nearest 0.0005 g (or 0.0005 mL).
3. Add conductance water (ca. 45 g) to bring solution level to top of vent holes in conductance probe. Begin continuous stirring without visible vortex.
4. Titrate with 0.1 N HCl to at least 3 mL beyond the beginning of the increased slope evidencing excess H<sup>+</sup> (see Figure A-2).
5. Determine the equivalence points from a graph of the titration curve (conductance vs. mL of titrant), and calculate the free amine and weak acid anions concentrations (see "Calculations"). If no bound amine was found in procedure A, perform an "Excess NaOH" titration (procedure C) before calculating free amine results.

C. Excess NaOH

1. (Same as Step A-1)
2. (Same as Step A-2)
3. Titrate with 0.1 N HCl to at least 3 mL beyond the beginning of the positive slope in the titration curve (see Figure A-3).
4. Determine the equivalence point from a graph of the titration curve (conductance vs. mL of titrant), and calculate the "excess NaOH" concentration (see "Calculations").

## CALCULATIONS

A. Bound Amine

Figure A-1 shows a typical titration curve for bound amine. The equivalence point is found, as illustrated, at the intersection of extrapolations of the linear portions of the titration curve. The concentration of bound amine is calculated as follows:

$$[B] = \frac{V * N}{W} \quad (1)$$

Where [B ] = Bound Amine concentration, meq/g  
 V = volume of NaOH titrant to the equivalence point, mL  
 N = Normality of NaOH titrant, meq/mL  
 W = weight of amine sample, g

Conversion of Bound Amine concentration from meq/g to wt% is accomplished by:

$$\text{wt\%} = (\text{meq/g}) * M / 10 \quad (2)$$

Where M = equivalent weight of the amine, mg/meq  
 = 119 for MDEA, 61 for MEA, 105 for DEA

#### B. Free Amine and Weak Acid Anions

Figure A-2 shows a typical titration curve for free amine and anions of weak acids. Two equivalence points are evident here. The first equivalence point is found, as illustrated, at the intersection of the extrapolations of the first two portions of the titration curve. The second equivalence point is found, as illustrated, at the intersection of the extrapolations of the second and third linear portions of the titration curve. The concentration of free amine is calculated as follows:

$$[F] = \frac{(V1 * Nh) + (Wac * Nac)}{W} - [Cex] \quad (3)$$

Where [F] = Free Amine concentration, meq/g  
 V1 = volume of HCl titrant to the first equivalence point, mL  
 Nh = Normality of HCl titrant, meq/mL  
 Wac = weight of acetic acid added, g  
 Nac = Normality of acetic acid, meq/g  
 W = weight of amine sample, g  
 [Cex] = excess NaOH concentration, meq/g

The concentration of titrable anions of weak acids is:

$$[A] = \frac{Nh *(V2 - V1) - (Wac * Nac)}{W} \quad (4)$$

Where [A] = titrable anion concentration, meq/g  
 V2 = volume of HCl titrant to the second equivalence point, mL

Conversion of meq/g concentration to wt% is accomplished by Equation 2, above. For weak acid anions, one must assume an equivalent weight, such as 60 (acetic acid) or 46 (formic acid).

### C. Excess NaOH

Figure A-3 shows a typical titration curve for excess NaOH. Only one equivalence point is shown here, although if the titration were continued, the remaining curve would look much like the free amine titration. The equivalence point is found, as illustrated, at the intersection of the extrapolations of the downward and upward sloping portions of the titration curve. The concentration of excess NaOH is calculated as follows:

$$[C_{ex}] = \frac{V_3 * N_h}{W} \quad (5)$$

Where  $C_{ex}$  = excess NaOH concentration, meq/g  
 $V_3$  = volume of HCl titrant to the equivalence point, mL

### Notes

1. For greater sensitivity, more amine solution may be taken. To reduce titrant consumption, take less amine solution. Amounts specified in the procedure are optimized for amine solutions containing on the order of 0.5 meq/g bound amine and 3 meq/g free amine. If less than 1 mL of titrant is required to the first endpoint, titrate a larger sample. Ambiguity of bound amine and excess OH<sup>-</sup> results can be resolved by titrating excess OH<sup>-</sup> 3 mL beyond the endpoint, then back-titrating with NaOH.
2. Acetic acid is added to enhance the segregation of free amine from the weak acid anions in the titration. If the amount of amine in the titration is less than 0.45 meq, the amine titration (from zero to V<sub>1</sub> in Figure A-2) will not be observed, and concentration calculation may be meaningless. Increase the amount of amine solution. For extremely weak free amine solutions (less than 0.45 meq in at least 50 g) the acetic acid addition may be eliminated, with potential loss of distinction between free amine and low concentrations of weak acid anions.

FIGURE A-1  
TYPICAL TITRATION CURVE for BOUND AMINE

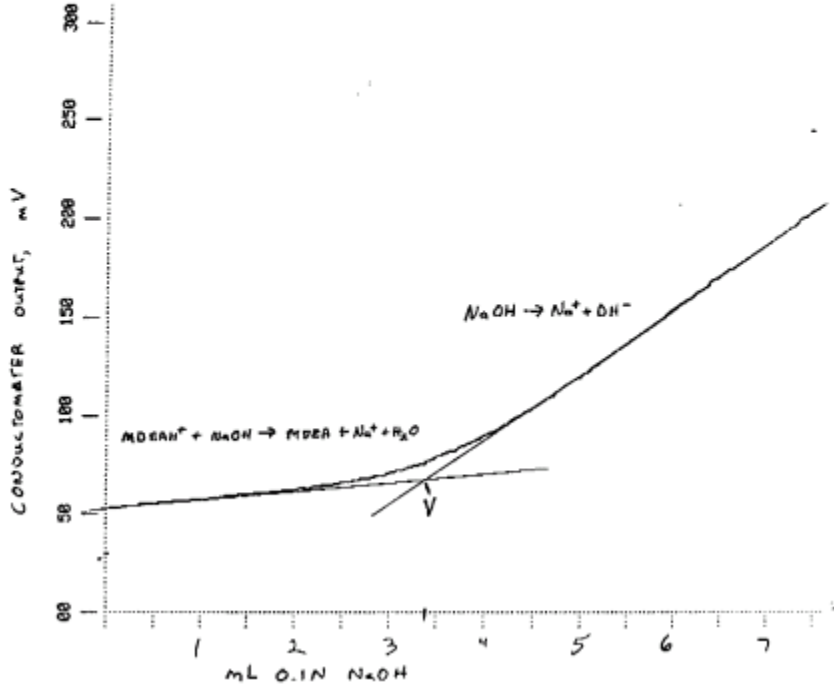


FIGURE A-2  
TYPICAL TITRATION CURVE for FREE AMINE and ANIONS

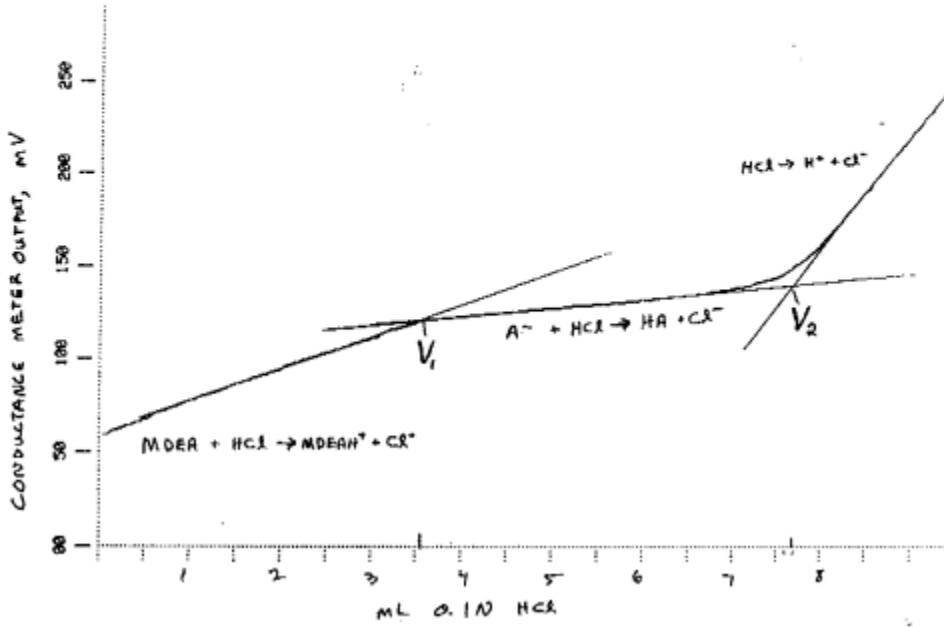


FIGURE A-3

TYPICAL TITRATION CURVE for EXCESS NaOH

