

# Determination of Betaine and Free Amine in Alkyldimethyl Betaine by Potentiometric Titrations<sup>1</sup>

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Two selective analytical methods are presented for the determination of betaine and free amine contents, respectively, in commercial alkyl dimethyl betaines. Both methods are based on titrations with potentiometric end point detection. The accuracy and precision are discussed.

**KEY WORDS:** Accuracy, alkyldimethyl betaine, analysis, betaine, detection limit, free amine, interlaboratory tests, potentiometry, precision, titrimetry.

Technical long-chain alkyldimethyl betaines generally contain low amounts of free amines. For the quantitation of such betaines, no analytical methods have been reported in the literature that can discriminate between betaines and free amines. The sum of betaine and free amine is determined in both titrimetric (1-3) and gravimetric methods (4). High-performance liquid chromatography (HPLC) methods (5-11) only deal with the separation of betaine mixtures, and non-betaine impurities are disregarded.

In this paper two titrimetric methods are presented for the selective determination of betaine and free amine in which the generally accompanying impurities, monochloroacetic acid and glycolic acid, do not interfere.

## EXPERIMENTAL PROCEDURES

**Materials.** All reagents were of analytical grade and used as received. Armoterac LB [ $\text{RN}^+(\text{CH}_3)_2\text{CH}_2\text{COO}^-$  ( $\text{R}=\text{C}_{12}/\text{C}_{14}$ ) 30% in water] and Armeen DMMCD [ $\text{RN}(\text{CH}_3)_2$  ( $\text{R}=\text{C}_{12}/\text{C}_{14}$ )] were supplied by Akzo Chemicals Division (Amersfoort, The Netherlands) and were used as received. Hexadecyl dimethyl betaine hydrochloric acid salt, [ $\text{C}_{16}\text{H}_{33}\text{N}^+(\text{CH}_3)_2\text{CH}_2\text{COOHCl}^-$ ] was obtained by recrystallization from Armoterac 16 [ $\text{C}_{16}\text{H}_{33}\text{N}^+(\text{CH}_3)_2\text{CH}_2\text{COO}^-$ , 30% in water-ethanol, Akzo Chemicals Division] in an ethanol-water mixture (3:1, vol/vol) at pH 1.5. As ascertained by <sup>1</sup>H nuclear magnetic resonance (NMR), this product is free from glycolic acid, monochloroacetic acid, free amine and ethanol; and contains 0.1% water as determined by Karl Fischer titration.

**Equipment.** All titrations are carried out on a Metrohm (Herisau, Switzerland) titro-processor E672 with Dosimat E635 with a 20-mL burette and a Metrohm combined glass reference electrode 6.0210.100 with 3 mole per liter LiCl in methanol as electrolyte.

**Betaine determination: analytical procedure.** The sample containing approximately 1 millimole betaine is weighed to the nearest 0.1 mg into a 250-mL beaker. Then 15 mL 2-propanol containing a small excess of hydrochloric acid is added to convert all compounds to their acidic form. Next, 150 mL methyl isobutyl ketone is

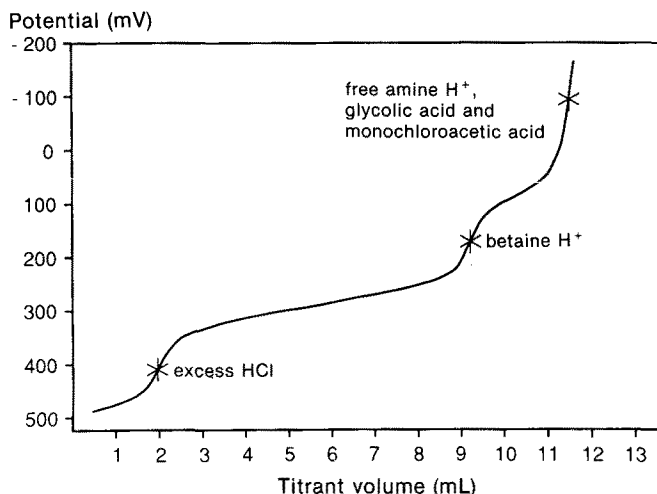


FIG. 1. Titration curve of betaine determination.

added. Sodium chloride present in the sample precipitates. As carbonic acid interferes, nitrogen is passed through the solution for 5 min. The solution is kept under a nitrogen blanket during the rest of the determination. The solution is then titrated with a standardized 0.1 N potassium hydroxide solution in ethanol.

The betaine content is calculated from the equation (see Fig. 1):

$$\text{betaine (\% m/m)} = \frac{V_1 - V_2}{m_1} \times N \times \frac{M}{10} \quad [1]$$

where  $V_1$  = titrant volume in mL up to the second potential jump (betaine  $\text{H}^+$ );  $V_2$  = titrant volume in mL up to the first potential jump (excess HCl);  $m_1$  = sample mass in g;  $N$  = normality of the potassium hydroxide titrant in milliequivalents per mL; and  $M$  = molar mass of the betaine in g per mole.

## RESULTS AND DISCUSSION

Figure 1 shows a typical titration curve when a commercial Armoterac LB sample is analyzed. The three potential jumps are attributed to the excess hydrochloric acid added, the betaine  $\text{H}^+$  and the free amine  $\text{H}^+$ , together with glycolic acid and monochloroacetic acid. This selectivity toward betaine has been proved by the addition of these particular compounds to the commercial betaine (see Table 1).

In the applied medium, the carboxylic acid functionality of the betaine has stronger acidic properties than the protonated amine and the carboxylic acids present.

The recovery has been studied by adding different amounts of pure hexadecyl dimethyl betaine hydrochloric acid salt to 700 mg of the commercial betaine (30% m/m). In Figure 2 the recovered amount of betaine is plotted against the added amount. An average recovery of 100.1%

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TABLE 1

## Selectivity of Betaine Determination

Added impurity	Betaine (% m/m)
None	29.38
5.4% m/m Free amine	29.41
2.2% m/m Glycolic acid	29.44
2.2% m/m Monochloroacetic acid	29.44

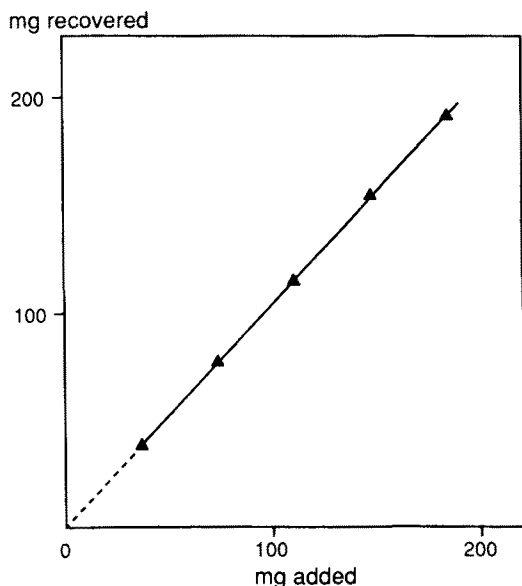


FIG 2. Recovery of betaine. Slope (mg/mg), 1.001 (SD = 0.005); intercept (mg), 0.1 (SD = 0.6); and correlation coefficient, 0.99996.

with a standard deviation of 0.5% is calculated from the slope of the curve. The intercept of 0.1 mg is not significant considering the standard deviation of 0.6 mg.

The method is linear in the tested region of 200–400 mg betaine. With varying the sample mass this covers contents from 10 up to 100% betaine in commercial samples.

The precision was investigated by means of an interlaboratory test between three laboratories with a fourfold analysis on a commercial sample C<sub>12</sub>/C<sub>14</sub> alkyldimethyl betaine (Table 2). The reproducibility (=2.83 S<sub>R</sub>) was 0.42% m/m at a level of 30.3% m/m.

**Free amine determination: analytical procedure.** The sample containing approximately 0.2 millimole of free amine with a maximum of 10 g is weighed to the nearest 1 mg into a 250-mL beaker. The sample is dissolved in 150 mL water/2-propanol mixture (1:1, vol/vol). As carbonic acid interferes, nitrogen is passed through the solution for 5 min. The solution is kept under a nitrogen blanket during the rest of the determination. Exactly 10.00 mL of a 0.02 molar tri-*n*-butyl amine solution in 2-propanol is added, ensuring a clear and distinct potential jump at a titrant volume of at least 2 mL. This improves precision and lowers the detection limit. Sodium hydroxide solution (0.1 N) in water is added in a small excess to be sure that all compounds are present in their basic form. The solution is then titrated with a standardized 0.1 N hydrochloric acid solution in water. A blank is carried

TABLE 2

## Interlaboratory Test Results for Betaine Determination (all results are in % mass by mass)

	Lab 1	Lab 2	Lab 3
Betaine content	30.20	30.28	29.96
	30.25	20.29	30.21
	30.45	30.29	30.34
	30.46	30.31	30.47
Mean value	30.34	30.29	30.25
Standard deviation	0.13	0.01	0.22

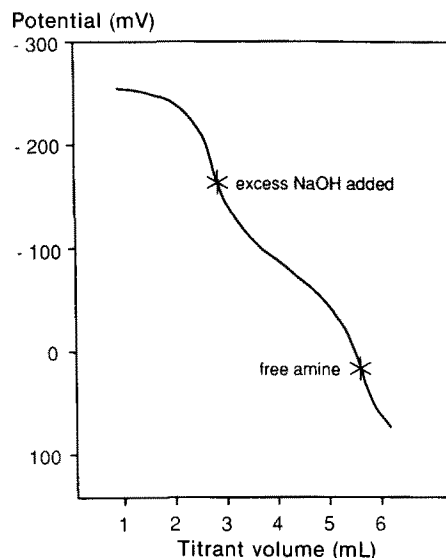


FIG 3. Titration curve of free amine determination.

out on the tri-*n*-butyl amine under exactly the same conditions.

The free amine content is calculated from the equation (Fig. 3):

$$\text{free amine (\% m/m)} = \frac{(V_3 - V_4) - (V_5 - V_6)}{m_2} \times N \times \frac{M}{10} \quad [2]$$

where  $V_3$  = titrant volume in mL up to the second potential jump (amine) for the sample solution;  $V_4$  = titrant volume in mL up to the first potential jump (excess NaOH) for the sample solution;  $V_5$  = titrant volume in mL up to the second potential jump (amine) for the blank solution;  $V_6$  = titrant volume in mL up to the first potential jump (excess NaOH) for the blank solution;  $m_2$  = sample mass in g;  $N$  = normality of the hydrochloric acid titrant in milliequivalents per mL; and  $M$  = molar mass of the free amine in g per mole.

**Results.** Figure 3 shows a typical titration curve when a commercial sample of Arnoteric LB is analyzed. The potential jumps correspond to the excess sodium hydroxide added and the free amine together with tri-*n*-butyl amine. The attribution of the potential jumps has been confirmed by addition of these particular compounds, which proves the selectivity of the method with respect to free amine (see Table 3). Glycolate, monochloroacetate

## SHORT COMMUNICATION

TABLE 3

## Selectivity of Free Amine Determination

Added impurity	Free amine (% m/m)
None	0.6
1.0% m/m Glycolic acid	0.6
1.0% m/m Monochloroacetic acid	0.6

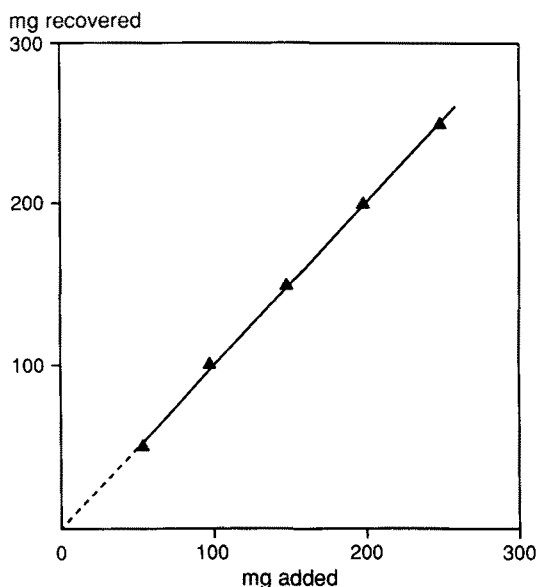


FIG. 4. Recovery of free amine. Slope (mg/mg), 0.994 (SD = 0.004); intercept (mg); 1.1 (SD = 0.6); and correlation coefficient, 0.99996.

and betaine potential jumps were expected at a titrant volume of 100 mL due to the big sample mass.

The recovery of free amine has been studied by addition of various amounts of C<sub>12</sub>/C<sub>14</sub> alkyldimethyl amine to 10 g of the betaine (Fig. 4). From the slope of the curve, the average recovery can be stated to be complete—99.4% m/m with a standard deviation of 0.4% m/m.

TABLE 4

## Interlaboratory Test Results for Free Amine Determination (all results in % mass by mass)

	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5
Free amine content	0.53	0.50	0.54	0.526	0.555
	0.54	0.50	0.55	0.544	0.555
	0.54	0.51	0.57	0.538	0.557
	0.55	0.52	0.58	0.551	0.564
Mean value	0.54	0.51	0.56	0.540	0.558
Standard deviation	0.008	0.010	0.018	0.011	0.004

An intercept of 1.1 mg corresponds with 0.01% free amine in the betaine. However, this intercept is not significant regarding its standard deviation of 0.6 mg. The method is linear in the tested region up to 250 mg free amine in 10 g of betaine. The latter corresponds with 2.5% m/m.

The precision was investigated by means of an interlaboratory test between five laboratories with a four-fold analysis on a commercial sample C<sub>12</sub>/C<sub>14</sub> alkyldimethyl betaine (Table 4). The reproducibility (=2,83 S<sub>R</sub>) was 0.065% m/m at a level of 0.54% m/m. The detection limit defined as three times the standard deviation of the blank is 0.02% m/m.

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