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The Analysis of Aliphatic Amine Mixtures; Determination of Tertiary Aliphatic Amines in the Presence of Primary and Secondary Amines and Ammonia

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Most of the methods proposed for determining tertiary aliphatic amines in the presence of primary and secondary amines have depended on the isolation and titration of unreacted tertiary amine after treatment of the mixture with nitrous acid.^{2,3} Mitchell, Hawkins and Smith⁴ determined primary and secondary amines in the presence of tertiary amines by acetylating the amines with a definite amount of acetic anhydride, hydrolyzing the excess acetic anhydride with a known amount of water, and determining the unused water with Karl Fischer reagent. Tertiary amine content of the sample could then be calculated from the total base value by difference.

Blumrich and Bandel⁵ have proposed a simple method for the direct determination of tertiary amines, namely, the acetylation of primary and secondary amines and ammonia in the mixture by means of acetic anhydride, followed by potentiometric titration of unreacted tertiary amine by means of perchloric acid in acetic acid. They reported application of the procedure to only one aliphatic amine mixture, composed of diethylamine and triethylamine.

Additional data have now been obtained to determine the applicability of Blumrich's original procedure to other aliphatic amines, and the method has been found to be generally applicable except in the cases involving secondary amines with the nitrogen atom attached to secondary alkyl groups. With these sterically-hindered molecules, more drastic acetylation conditions are necessary. In testing several aliphatic amines, it was found that by acetylating under more vigorous conditions (reflux for one hour instead of allowing the mixture to stand three hours at room temperature), such sterically-hindered secondary amines are quantitatively acetylated. It was also observed that under these conditions in the absence of acetic acid in the reaction mixture, certain tertiary amines are destroyed at a significant rate. However, they undergo only slight, if any, deterioration when acetic acid is present in the acetic anhydride in amounts equivalent to the amines in the mixture. Water in the sample apparently does not interfere in the procedure, since the presence of as much as two grams of water does not prevent complete acetylation.

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(2) E. Briner and J. Gandillon, *Helv. Chim. Acta*, **14**, 1283 (1931).

(3) K. G. Mizuch and A. Ya. Savchenko, *Org. Chem. Ind. U. S. S. R.*, **7**, 24 (1940).

(4) J. Mitchell, Jr., W. Hawkins and D. M. Smith, *THIS JOURNAL*, **66**, 782 (1944).

(5) K. G. Blumrich and G. Bandel, *Angew. Chem.*, **54**, 374 (1941).

Analytical Method

Reagents and Apparatus.—The standard 0.1 *N* acid is prepared by mixing the required amount of C. P. 70% perchloric acid with glacial acetic acid. The solution is standardized against anhydrous sodium carbonate (heat C. P. material at 400–450° for three to four hours) dissolved in acetic acid and titrated potentiometrically or to the crystal violet end-point.

A potentiometric titrometer of the direct-reading type, such as the Beckman Model M or the Precision-Shell,⁶ using glass and calomel electrodes, is convenient and very satisfactory for use in this analysis.

General Procedure.—A sample weighing not more than 2 g. and containing no more than 1 g. of water is added to 20 ml. of acetic anhydride containing 2 ml. of acetic acid. The mixture is allowed to stand three hours at room temperature. Thirty ml. of acetic acid is added, and the mixture is titrated potentiometrically with 0.1 *N* perchloric acid in acetic acid.

Special Procedure (for use with sterically-hindered secondary amines).—A sample similar to the one above is added to the acetylating mixture of 20 ml. of acetic anhydride and 2 ml. of acetic acid. This mixture is refluxed gently for one hour. It is then added to 30 ml. of acetic acid in a titration beaker and titrated potentiometrically as above.

Experimental

Representative data obtained by application of the method to individual amines are tabulated in Table I. In

TABLE I
APPLICATION OF THE METHODS TO INDIVIDUAL AMINES

Amines present ^d	Amine content of sample eq. × 10 ^{2a}	Unacetylated amine found, eq. × 10 ³		Unacetylated amine found, mole % of amine present
		Acetylated at room temp. 3 hours	Acetylated under reflux one hour	
1,3-Dimethylbutylamine	7.41	0.00		0.0
1,3-Dimethylbutylamine	37.1		0.00	.0
Dimethylamine	6.00	.00		.0
Diisopropylamine ^b	12.55	2.80		22.3
Diisopropylamine ^b	35.7		.00	0.0
bis-(1,3-Dimethylbutyl)-amine ^b	8.06	1.72		21.3
bis-(1,3-Dimethylbutyl)-amine ^b	20.2		.00	0.0
Triallylamine ^c	2.157	2.063		95.6
Triallylamine ^c	2.193		2.091	95.3
Tri- <i>n</i> -butylamine ^b	1.672		1.630	97.5
Diisopropyl- <i>n</i> -propylamine ^b	1.468		1.457	99.2

^a Calculated amine content made on basis of titratable nitrogen content of each amine component used. ^b Purified laboratory samples. ^c In another test with a reaction period of forty-six hours at 25° instead of three hours, 95.5% recovery was obtained. Close correlation between results obtained at three and forty-six hours indicates the presence of 4.5% secondary (or primary) amine in the redistilled triallylamine sample. ^d Diethylamine, isopropylamine, *n*-butylamine, di-*n*-butylamine, allylamine, diallylamine, ethanolamine and diethanolamine were all quantitatively acetylated in three hours at room temperature.

(6) C. J. Penther and F. B. Rolfsen, *Ind. Eng. Chem. Anal. Ed.*, **15**, 337 (1943).

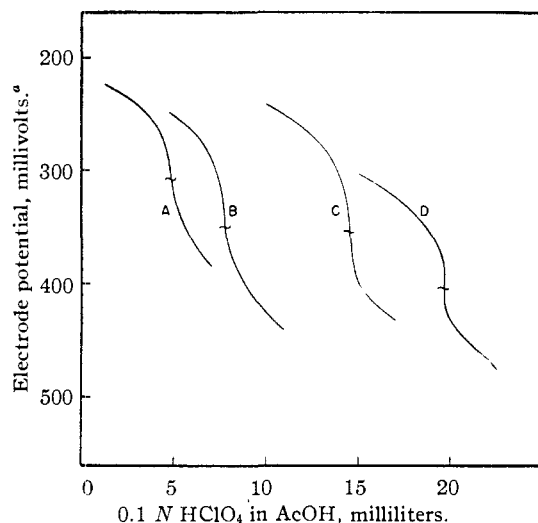


Fig. 1.—Typical potentiometric titration curves of tertiary amines in acetylated amine mixtures.

Composition of mixtures		
	A, %	C, %
Diisopropyl- <i>n</i> -propylamine	3.46	51.7
Diisopropylamine	8.1	24.9
Isopropylamine	38.8	23.4
Ammonia	1.2	
Water	48.4	
	B, %	D, %
Tri- <i>n</i> -butylamine	4.49	40.7
Di- <i>n</i> -butylamine	11.5	29.1
<i>n</i> -Butylamine	21.8	26.6
Ammonia	0.8	0.0
Water	61.4	3.6

^a Zero on electrode potential scale is equivalent approximately to a *pH* of 7 when the electrode system is used in aqueous solution.

addition to those amines included in the table, allylamine, isopropylamine, *n*-butylamine, diethylamine, diallylamine, di-*n*-butylamine, ethanolamine, and diethanolamine were found to be completely acetylated when either method of acetylation was applied.

A sample of diisopropyl-*n*-propylamine treated one hour under reflux with acetic anhydride alone analyzed only 90.6%, whereas with acetic acid present a value of 99.2% was obtained with one hour of reflux and 98.8% with sixteen hours of reflux. Tri-*n*-butylamine treated one hour under reflux by the prescribed method gave a value of 97.5% of the titratable nitrogen value and with sixteen hours under reflux 96.4% of the titratable nitrogen value.

The two methods were also applied to various known mixtures. Typical results on five such samples are listed in Table II and Fig. 1 illustrates the titration curves obtained with four of them. In the presence of large amounts of amides, the end-point is often slightly buffered,

TABLE II
APPLICATION OF METHODS TO KNOWN MIXTURES

Mixture components	Detns.	Sample comp., ^c %w	Tertiary amine found, %w
Diisopropyl- <i>n</i> -propylamine		3.46	3.51 ± 0.05 ^a
Diisopropylamine		8.1	
Isopropylamine	3	38.8	
Ammonia		1.2	
Water		48.4	
Diisopropyl- <i>n</i> -propylamine		51.7	51.1 ± 0.05 ^a
Diisopropylamine	3	24.9	
Isopropylamine		23.4	
Tri- <i>n</i> -butylamine		4.49	4.64 ± 0.04 ^b
Di- <i>n</i> -butylamine		11.5	
<i>n</i> -Butylamine	3	21.8	
Ammonia		0.8	
Water		61.4	
Tri- <i>n</i> -butylamine		40.7	40.4 ± 0.12 ^b
Di- <i>n</i> -butylamine	3	29.1	
<i>n</i> -Butylamine		26.6	
Water		3.6	
Triethanolamine	1	73.7	72.2 ^b
Diethanolamine		17.9	
Monoethanolamine		8.4	

^a Acetylated under reflux for one hour. ^b Acetylated at room temperature for three hours. ^c Based on titratable nitrogen values of the components.

but when the sample consists of essentially pure tertiary amine, the end-point is sharp, and crystal violet may then be used as a colorimetric indicator to supplant the somewhat slower potentiometric procedure. It is recommended, however, that use of the indicator in analyzing any particular mixture should first be tested by utilizing the indicator and potentiometric titration simultaneously on a typical sample.

Summary

Data are presented indicating the extent of applicability of the method proposed by Blumrich and Bandel for the determination of tertiary aliphatic amines. The method is found not satisfactory in the presence of certain sterically hindered secondary aliphatic amines, and a modification of the method is proposed which seems to obviate this difficulty so that the method as modified is applicable to aliphatic amine mixtures in general. The procedure involves no compound separations, the analysis being made on the original sample directly. Ammonia and water in the amine mixtures do not interfere.

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