• Technical

Determination of Primary and Secondary Fatty Aliphatic Amines in the Presence of Large Amounts of Nitrile by Near-Infrared Spectroscopy

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ABSTRACT

There are numerous methods proposed for determination of primary, secondary and tertiary amines. Most seem to be lengthy, inaccurate and unsuitable for small samples. Previous spectroscopic methods based on near-infrared spectroscopy for determination of aliphatic and aromatic amines are not applicable for samples containing more than 10% nitrile. A simple method based on near-infrared spectroscopy has been developed, and is presented, for determination of primary and secondary fatty aliphatic amines in the presence of 0-100% nitrile.

INTRODUCTION

High molecular weight aliphatic amines are used extensively in many industries. In the manufacture of these aliphatic amines, fatty acids obtained from animal fat and tall oil are often used as feed materials. The final product, which should be primary amine, is obtained by hydrogenating the nitrile that is produced by ammoniation of the fatty acids. The nitrile hydrogenation is done gradually in a series of reactors over Raney nickel or other similar catalyst until theoretically 100% amine is in the final tank. Therefore the composition of the mixture in any step of the process is of considerable importance in following the progress of the hydrogenation and thereby imposing the proper conditions of each reactor.

Thus there is a great need for a simple analytical method for determination of primary and secondary amines in the presence of 0-100% fatty nitrile. Many analytical methods other than near-infrared spectroscopy have been proposed for determination of primary, secondary and tertiary

TABLE I

Determination of Primary and Secondary Fatty Amines in the Presence of Fatty Nitrile

Reference		Chloroform		Nitrile	
Blend	Amine	g/liter added	g/liter found	g/liter added	g/liter found
90% Amine 10% Nitrile	Primary	0.00	0.00	0.00	0.00
	Secondary	13.50	13.56	13.50	13.54
	Primary	4.50	4.57	4.50	4.55
	Secondary	9.00	9.07	9.00	8.98
	Primary	9.00	9.06	13.50	13.51
	Secondary	4.50	4.56	0.00	0.00
70% Amine 30% Nitrile	Primary	0.00	0.00	—	—
	Secondary	10.50	11.10	—	—
	Primary	10.50	11.10	—	—
	Secondary	0.00	0.00	—	—
	Primary	4.50	5.10	—	—
	Secondary	6.00	6.30	—	—
60% Amine 40% Nitrile	Primary	—	—	0.00	0.00
	Secondary	—	—	9.00	9.01
	Primary	—	—	6.00	6.02
	Secondary	—	—	3.00	3.01
	Primary	—	—	9.00	9.01
	Secondary	—	—	0.00	0.00
50% Amine 50% Nitrile	Primary	0.00	0.00	0.00	0.00
	Secondary	10.00	11.53	10.00	10.02
	Primary	6.00	7.73	5.00	5.01
	Secondary	4.00	5.62	5.00	5.01
	Primary	10.00	10.81	10.00	10.01
	Secondary	0.00	0.00	0.00	0.00
10% Amine 90% Nitrile	Primary	0.00	0.00	0.00	0.00
	Secondary	4.00	5.62	4.00	4.01
	Primary	2.00	3.65	2.00	2.03
	Secondary	2.00	3.75	2.00	2.02
	Primary	4.00	5.73	4.00	3.99
	Secondary	0.00	0.00	0.00	0.00

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TABLE II

Average Errors Found in Analysis of Known Blends of Amine and Nitrile With and Without Nitrile in the Reference

Blend	Amine	Average error With nitrile	Average error Without nitrile
100% Amine mixture	Primary	+0.013	+0.001
0% Nitrile	Secondary	+0.010	+0.010
90% Amine mixture	Primary	+0.011	+0.061
10% Nitrile	Secondary	-0.012	+0.070
80% Amine mixture	Primary	+0.006	+0.121
20% Nitrile	Secondary	+0.014	+0.009
70% Amine mixture	Primary	+0.001	+0.431
30% Nitrile	Secondary	+0.008	+0.437
60% Amine mixture	Primary	+0.009	+0.903
40% Nitrile	Secondary	+0.008	+0.965
50% Amine mixture	Primary	+0.006	+1.584
50% Nitrile	Secondary	+0.005	+1.587
40% Amine mixture	Primary	+0.009	+1.670
60% Nitrile	Secondary	+0.008	+1.691
20% Amine mixture	Primary	+0.010	+1.645
80% Nitrile	Secondary	+0.007	+1.677
10% Amine mixture	Primary	+0.010	+1.660
90% Nitrile	Secondary	+0.007	+1.625

amines; most of them seem lengthy, inaccurate and unsuitable for use with rather small samples (1-5).

Near-infrared methods for determination of primary and secondary aliphatic and aromatic amines are not actually a new development. Liddel and Wulf (6) calculated absorptivities at the absorption maxima of ca. 1.5 μ due to N-H stretching in a number of primary and secondary aliphatic and aromatic amines.

Holman and Edmonson (7) measured the absorption of a series of fatty acids and other lipids and assigned bands for several organic structures.

Whetsel et al. (8-10) have studied mixtures of primary and secondary aromatic amines, the first overtone -OH, -NH stretching of N-alkyl and N-alkyl-N-hydroxyalkyl aromatic amines.

Goddu and Delker (11) organized a spectra-structure correlation chart for the near-infrared region. This chart showed bands at about 1.50-1.55 μ and 2.00-2.05 μ for primary aliphatic amines and 1.53 and 1.55 μ for secondary aliphatic amines.

In 1963 Lohman and Norteman (12) developed a method for determination of primary and secondary amines in the presence of tertiary amines by near-infrared spectroscopy. Observation of their data will show that mixtures containing more than 10% nitriles and other substances showed on interference in the amine determination in that mixture.

This research has extended the spectroscopic method previously developed (12) by showing it is applicable for the entire range from 0-100% amine and in the presence of large amounts of nitrile in a mixture of fatty aliphatic amines.

EXPERIMENTAL PROCEDURES

Characteristic primary and secondary amine absorptions in the near-infrared region of the spectrum were used to determine quantitatively the concentration of each in known solutions, also containing nitrile.

Mixtures of primary and secondary amines plus nitrile were made up and run on the Beckman DK-2A spectrophotometer, first using a reference of chloroform and next a reference of nitrile diluted in chloroform. Then the absorption maxima at 2025 mμ and 1551 mμ were used to calculate the percentages of primary and secondary amine present.

Apparatus and Reagents

Apparatus and reagents were: (a) chloroform, spectrophotometric grade; (b) fused silica cells, 5.0 cm path length; (c) 50 ml volumetric flasks; (c) primary amine Armour's Armeen (D 77% oleyl amine or equivalent, 8% other unsaturated primary amines, 15% saturated primary amines (98% minimum purity for primary amine); (e) secondary amine Armour's Armeen 2HT 63% stearyl amine or equivalent, 35% other saturated secondary amines, 2% unsaturated secondary amine (95% minimum purity for secondary amine); (f) nitrile, Armour's Arneed OD 78% oleyl nitrile or equivalent, 22% other nitriles. All were used as supplied.

Calibration

Primary Amine. A series of standard solutions of the primary amine was prepared in 50 ml volumetric flasks containing 0.75000 g of nitrile in chloroform, corresponding to 0, 5, 10, 15, and 20 g/liter amine. Using the sample containing 0.7500 g nitrile and 0.0000 g amine as a reference, the spectrum was scanned from 2100 mμ to 1950 mμ for each of the amine samples using a 5 cm fused silica cell and the following instrument settings:

Speed	20 (7.5 mμ/sec)
Scale	Absorbance
Period	0.2
Sensitivity	Sufficient to give a slit of 0.04 mm at 2.0 μ with 0.750 g nitrile diluted to 50 ml with chloroform in the reference and sample beams
Photomultiplier	2-X

For each sample the absorbance was read at 2025 mμ and 1551 mμ as maxima and the net absorbance was calculated. These absorbance values were plotted vs. concentration of amine to obtain calibration curves for the primary amine at 2025 mμ and 1551 mμ respectively.

Secondary Amine Calibration. A series of standard solutions of secondary amine plus nitrile was prepared in 50 ml volumetric flasks as described for primary amine.

The 5 cm cell was filled and the spectrum was scanned from 1600 mμ to 1500 mμ, using the sample containing 0.7500 g nitrile and 0.0000 g amine as the reference and using the instrument settings as described for primary amine. For each sample the net absorbance was calculated at 1551 mμ and plotted vs. concentration to obtain the calibration curve for secondary amine at 1551 mμ.

Procedure

In a 50 ml beaker a sufficient amount of the amine and nitrile mixture was weighed to give a total concentration of 15-20 g/liter (more concentrated for low purity amine), dissolved in ca. 20 ml chloroform, transferred quantitatively to a 50 ml volumetric flask and diluted to the mark with chloroform.

With the sample in one 5 cm cell and 15-20 g/liter nitrile dissolved in chloroform as reference, the spectrum was scanned from 2100-1950 mμ and from 1600-1500 mμ, using the instrument settings described under Calibration. The value of the net absorbance was taken at 2025 mμ and the calibration curve previously prepared for primary amine was used at 2025 mμ, to obtain the concentration of primary amine in g/liter.

The concentration obtained above for the primary amine (g/liter was converted to its corresponding absorbance at 1551 mμ using the calibration curve previously prepared for primary amine at 1551 mμ. This absorbance value was subtracted from the net absorbance found at 1551 mμ due to secondary amine. The calibration curve prepared for secondary amine at 1551 mμ was used to convert this absorbance value to concentration (g/liter).

RESULTS AND DISCUSSION

This method has extended the method developed by Lohman and Norteman (12) to include the range of fatty aliphatic amines from 0-100% and modified it to make it applicable in the presence of large amounts of nitrile.

Preliminary information acquired at the beginning of this research indicated a large error in the determination of primary and secondary aliphatic amines when the mixture consisted of more than 10% nitrile. Some of these data are presented in Table I.

It was observed that the error could be decreased as the nitrile concentration in the reference cell neared the nitrile concentration in the sample cell and at the point of equality the error became constant as shown in Table I. Therefore, the lowest error in the determination is obtained when the nitrile concentration in the reference cell is equal to or greater than the nitrile concentration in the sample cell.

The method resulting from this research has been used in the determination of primary and secondary fatty aliphatic amines in mixtures of amine with 0-100% nitrile present. Comparative data are presented in Table II which indicate that in order to obtain accurate results when more than 10% nitrile is present in the sample, the nitrile concentration in the reference cell must be equal to or greater than the nitrile concentration in the sample.

It is suggested that the modified near-infrared method developed in this research is a simple procedure and requires only about one-third the time required to determine primary amine in such a mixture by vacuum distillation.

ACKNOWLEDGMENT

This research was supported through funds from the McIntire-Stennis Cooperative Forestry MRP-2 Research Project of the School of Forestry of Louisiana Tech University. Samples of amine and nitrile were obtained from Armour Industrial Chemical Company.

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[Received July 7, 1971]