inal tips of virgin female gypsy moths are attractive to males. The attractiveness was markedly increased by hydrogenation. The attractant remained in the neutral fraction after saponification and it reacted with phthalic anhydride. It was recovered from the phthalic acid ester by saponification. The attractant is specific for the male gypsy moth. None of several synthetic materials tested showed any attractiveness.

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[CONTRIBUTION FROM THE AMMONIA DEPARTMENT, E. I. DU PONT DE NEMOURS & CO., INC.]

Analytical Procedures Employing Karl Fischer Reagent. XII. The Determination of Primary Amines[1]

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The determination of primary amines with few exceptions has long been limited to reaction with nitrous acid, which often is not satisfactory. Occasionally the reaction between primary amine and aldehyde has been used for specific purposes, including reactions with formaldehyde,[2] for the identification of aromatic amines[3] and for the separation of primary aryl amines and secondary alkylaryl amines with benzaldehyde–sodium bisulfite.[4] Colorimetric methods for the identification of primary amines based on reaction with anhydro-bis-indanediones[5] and for monoethanolamine[6] have been reported. None of these last techniques are generally applicable to the determination of the primary amino group.

In the present investigation a technique has been developed based on the Schiff type reaction

$$RNH_2 + C_6H_5CHO \longrightarrow RN{=}CHC_6H_5 + H_2O$$

The water formed from the rapid quantitative reaction in the presence of pyridine between the amine and aldehyde is titrated with Karl Fischer reagent, after the excess aldehyde has been removed by means of the cyanhydrin reaction.[7]

The new procedure is applicable to aliphatic, alicyclic and aromatic primary amines and also amino alcohols which do not contain a secondary amino nitrogen group. Heterocyclic secondary amines interfere.

Combined with the acetylation technique for primary plus secondary amine,[8] the present method permits the estimation of secondary amine. When a total base titration is included, these procedures offer a means for determining rapidly and precisely the primary, secondary and tertiary amine content of mixtures.

Experimental

Analytical Procedure.—The sample, containing up to 0.1 equivalent of primary amine, is weighed into a 100-ml. volumetric flask about one-third filled with dry pyridine. After dilution to the mark with more pyridine, a 10-ml. portion is transferred to a 250-ml. glass-stoppered volumetric flask. Three ml. of benzaldehyde[9] is added, the flask stoppered and, together with a blank, placed in a 60° bath. After thirty minutes the flasks are removed and allowed to cool spontaneously to room temperature. The flasks are transferred to a well-ventilated hood. About 0.2 g. of dry sodium cyanide and 30 ml. of 6% hydrogen cyanide in pyridine are added. The flasks are shaken vigorously for about one minute[10] and then set aside in the hood for forty-five minutes. At the end of this time the mixture is titrated with Fischer reagent[11] to the usual visual end-point.[12]

The water found after correction for that present in the blank and original sample is equivalent to the amount of primary amine in the sample. Free water is best obtained by titrating the original sample in acetic acid solution.

Analytical Results

A group of seventeen widely different primary and primary–secondary amines was analyzed by the new method and reported in Table I. With the exception of *p*-bromoaniline, which was recrystallized from chloroform, the trade products were used without further purification. The precision and accuracy are usually within ±0.2%.

Results for *p*-bromoaniline were precise but consistently about 5% low as compared with the value obtained by the acetylation method. Urea and methyl urea reacted to the extent of about 10% on the basis of one mole of water formed per mole. This value would be doubled if the disubstitution product were formed.[13]

Amino alcohols containing only primary amine groups react quantitatively. This reaction, presumably, might follow one of two courses, either normal imine formation or condensation involving both the amine and hydroxyl to form a substituted oxazine type compound.[14] In this case the

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(1) Presented in part before the Division of Analytical and Micro-Chemistry at the 106th meeting of the American Chemical Society, Pittsburgh, Pa.

(2) Yul'chevskaya, *et al.*, *Lab. Prakt.*, **16**, 6 (1941).

(3) Schoorl, *Pharm. Weekblad*, **77**, 1381 (1940).

(4) Ferry and Buck, THIS JOURNAL, **58**, 2444 (1936).

(5) Wanag, *Z. anal. Chem.*, **21**, (1938).

(6) Shupe, *J. Assoc. Off. Agr. Chem.*, **24**, 754 (1941).

(7) Bryant, Mitchell and Smith, THIS JOURNAL, **62**, 3504 (1940).

(8) Mitchell, Hawkins and Smith, *ibid.*, **66**, 782 (1944).

(9) Either freshly distilled or acid-free benzaldehyde inhibited with about 0.1% hydroquinone is preferred. Results with benzylamine were only 95% quantitative using benzaldehyde containing about 10% benzoic acid.

(10) This shaking is required to initiate the cyanhydrin reaction since the sodium cyanide catalyst is insoluble in the pyridine.

(11) Preferably in a well-ventilated hood since the mixture contains excess hydrogen cyanide.

(12) This titration should be fairly rapid. The first sharp end-point should be taken, for occasionally some fading may be observed after standing a few minutes.

(13) Schiff, *Ann.*, **291**, 368, 370, 371 (1896).

(14) Kohn, *Monatsh.*, **26**, 956 (1905), isolated 4,6,6-trimethyl-2-phenyltetrahydrometoxazine after treating benzaldehyde with 2-hydroxy-2-methylpentylamine 4.

TABLE I

ANALYTICAL DATA FOR PRIMARY AMINES

Substance	% Amine (other methods)	Analysis (using Fischer reagent), %		
		Amine	Water	Total
Propylenediamine[b]		(2)[a] 86.3 ± 0.3	14.1	100.4
n-Butylamine		(6) 98.2 ± 0.2	1.7	99.7
Diethylenetriamine[b]		(4) 96.7 ± 0.1	1.3	98.0
Hexamethylenediamine[c]		(4) 97.2 ± 0.1	2.7	99.9
Decamethylenediamine[c]		(2) 97.0 ± 0.5		
Laurylamine[c]	98.1[g]	(2) 98.2 ± 0.2	0.6	98.8
Cyclohexylamine	100.2[g]	(4) 99.7 ± 0.2	0.3	100.0
2-Aminomethylcyclopentylamine		(2) 94.2 ± 0.3	5.4	99.6
o-Aminodicyclohexyl[d]		(2) 94.2 ± 0.2	0.1	94.3
Aniline[e]	98.8[h]	(2) 98.8 ± 0.1	.1	98.9
m-Aminophenol		(2) 99.5 ± 0.1	.0	99.5
p-Bromoaniline	99.4[h]	(6) 94.8 ± 0.3	.0	94.8
p-Phenylenediamine	99.6[h]	(4) 99.9 ± 0.0	.0	99.9
Benzylamine	92.8[g]	(5) 92.5 ± 0.2	.7	92.9
Toluidine[c]		(2) 97.1 ± 0.3	.0	97.1
o-Aminodiphenyl[d]		(2) 92.6 ± 0.2		
β-Naphthylamine[f]	97.3[h]	(4) 97.2 ± 0.1	0.0	97.2

[a] Figures in parentheses represent number of individual determinations. [b] Carbide and Carbon Chemical, 85%. [c] Du Pont. [d] Monsanto. [e] Arthur H. Thomas Co. [f] J. T. Baker; all others Eastman Kodak Co. Chemicals. [g] By titration to brom phenol blue. [h] By acetylation according to preceding paper of this series.[8]

exact mechanism of the reaction was not established, since by either route one mole of water is formed from each mole of amino alcohol present in the sample. Experimental data obtained on several amino alcohols are given in Table II.

TABLE II

ANALYTICAL DATA FOR PRIMARY AMINO ALCOHOLS

Substance	Found, wt. %
Monoethanolamine[a]	100.1 ± 0.2
2-Amino-2-methylpropanol	91.1 ± 0.2
2-Amino-2-methyl-1,3-propandiol	91.6
2-Amino-1-butanol	88.9 ± 0.2
Tris-(hydroxymethylaminomethane)	96.1 ± 0.2

[a] Purified Carbide and Carbon chemical; all others Commercial Solvents materials.

Aliphatic and aromatic secondary amines and tertiary amines do not interfere to any appreciable extent. Negative results were obtained on di-isobutylamine, methylaniline, diphenylamine, carbazole, triethanolamine and tri-isopropanolamine. Values of 1.5 and 2.0%, respectively, on diethyl and di-*n*-butylamine may have been due to primary amine impurity.

Interfering Substances.—Amino alcohols having a secondary amine group usually react nearly quantitatively. Following the conditions of the general procedure diethanolamine gave one mole of water per mole of amine; di-isopropanolamine and hydroxyethylethylenediamine gave 0.9 and 1.8 moles of water, respectively. A compound boiling at 160° (10 mm.) was isolated after reaction of diethanolamine with benzaldehyde. Elemental analysis indicated the compound $C_{11}H_{15}NO_2$. The molecular weight found was 180 as compared with 193 calculated. Both tertiary amino nitrogen and some free hydroxyl suggested that possibly this type of amino alcohol also condenses with benzaldehyde to form a heterocyclic ring compound.

Heterocyclic amines react with benzaldehyde to form the N,N′-benzaldiimines, eliminating one mole of water for every two moles of amine. N,N′-Benzaldipiperidine, melting at 83°, was isolated as the product from the reaction of piperidine with benzaldehyde, in the molar proportions used in the analytical procedure. The literature values for the melting point of this material vary from 78 to 81°.[15,16,17] Apparently both piperazine and morpholine react in the same manner, for in both cases the ratio of water found to amine added was one to two.

Summary

1. A quantitative procedure for the direct determination of primary amines has been described. It is based on titration with Karl Fischer reagent of the water formed from the reaction of the amine with benzaldehyde.

2. Quantitative results have been reported for sixteen primary amines and five primary amino alcohols.

3. The interference of secondary amino alcohols and heterocyclic secondary amines has been discussed.

4. The new procedure combined with the acetylation technique, described in the previous paper of this series, and a total base titration affords a means of rapidly and precisely analyzing mixtures of primary, secondary and tertiary amines.

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[15] Laun, *Ber.*, **17**, 678 (1884).

[16] Ehrenberg, *J. prakt. Chem.*, [2] **36**, 130 (1887).

[17] Lachowicz, *Monatsh.*, **9**, 698 (1888).