In a series of seven analyses in the range of from 0.14 to 3.4 parts per million of lead the average error was 1.5 per cent and the maximum error was 6.0 per cent, using cider containing known added amounts of lead. In this case six separate differences in line lengths were averaged to give each of the seven points on the working curve. Eighteen samples of commercial cider were examined, and all contained minute amounts of lead (Table I). Five samples which were examined only to an accuracy of less than 1 p. p. m. of lead are not included in the table.

ANALYSIS OF VINEGAR. Twenty-five cubic centimeters of vinegar were evaporated to dryness in a platinum dish, and the residue was dissolved in 0.5 cc. of double-distilled hydrochloric acid containing 1 mg. of bismuth per cc. The well-mixed solution of the vinegar residue was divided equally among three cupped graphite electrodes which had previously been treated with one drop of lead-free kerosene to prevent the solution from soaking into the electrodes. The detormination was thon envirid out as in into the electrodes. The determination was then carried out as in the cider method.

In one series of twelve analyses, using vinegar containing known added amounts of lead in the range of from 0.4 to 1.2 p. p. m., the average error was 7 per cent and the maximum error was 20 per cent. In another series of six analyses in the range of from 0.08 to 0.4 p. p. m. of lead the average error was 9 per cent and the maximum error was 25 per cent. Fifty-six samples of commercial vinegar were examined, and all but two, both distilled and spirit vinegar, contained lead (Table I). The geometric mean is nearer the median than is the arithmetic mean, indicating the geometric nature of the series.

The lead tolerance adopted by the United States Department of Agriculture under the old food and drug law was 0.025 grain per pound, which is equivalent to 3.5 p. p. m. Only one of these samples exceeded that figure. The next lower result was 1.8 p. p. m. or approximately one half of the tolerance.

The lead content of the cider was on the average less than that of the cider vinegar. There are two possible explanations. The cider was made from New England apples which do not require so much spraying as do western apples, but the vinegar was not exclusively a Massachusetts product. It is customary in the manufacture of sweet cider prior to placing it on the market to filter the apple juice through sand or some other type of filter which may remove some of the lead, but in the manufacture of vinegar this filtration is not always carried out. Furthermore, vinegar is a good solvent for lead in paint, metals, etc., with which it may come in contact during processing.

PRESENTED in part before the Division of Agricultural and Food Chemistry at the 100th Meeting of the American Chemical Society, Detroit, Mich.

A Method for the Identification of Nitriles

HAROLD B. CUTTER AND MICHAEL TARAS, Wayne University, Detroit, Mich.

CEVERAL methods have been proposed for the identifica- \triangleright tion of nitriles (1, 2, 3). The authors have found that adaptation of the well-known method of reduction of nitriles to primary amines by sodium and absolute alcohol gives a practical method for the identification of aliphatic nitriles. Aromatic nitriles do not give such good results, but this class can usually be readily determined by hydrolysis to the corresponding amide or acid.

Procedure

A solution of 1 cc. (0.8 to 1.0 gram) of the nitrile in 20 cc. of absolute alcohol is placed in a 200-cc. round-bottomed flask fitted with a reflux condenser. (It is essential that the alcohol be abwith a reflux condenser. (It is essential that the alcohol be ab-solute, otherwise considerably less derivative is obtained.) The flask is immersed to the neck in a water bath heated to 50° to 60° C. Fresh, finely cut sodium (1.5 grams) is added gradually through the top of the condenser as rapidly as possible without allowing the reaction to become too vigorous. When all the sodium has reacted (10 to 15 minutes) the reduction is complete. The mixture is cooled to 20° , and 10 cc. of concentrated hydro-chloric acid are added in small portions through the top of the condenser. Care is necessary on account of the spattering which takes place when the acid strikes the strongly alkaline mixture. The reflux condenser is disconnected, the system is set un for

The reflux condenser is disconnected, the system is set up for The reflux condenser is disconnected, the system is set up for ordinary distillation, and 20 cc. of alcohol are distilled into a graduated cylinder. The residue in the flask is cooled to 20° and a solution of 6 grams of sodium hydroxide in 6 cc. of water is cautiously added. The reaction at this point is violent, and care is necessary to avoid loss of amine by volatilization. The flask is swirled to ensure mixture of the ingredients and then rapidly reconnected to the condenser. Using a smoky flame the flask is heated until the contents are nearly dry, catching the distillate in a 50-cc. Erlenmeyer flask containing 3 cc. of water. The condenser should be fitted with an adapter dipping beneath the surface of the water in the flask. the surface of the water in the flask.

If the original substance was a nitrile, the distillate will be alkaline at this point.

Phenylisothiocyanate (0.5 to 1.0 cc.) is then added to the distillate, and the mixture vigorously shaken for 2 or 3 minutes. If no derivative forms on shaking, scratching the walls of the Erlenmeyer and cooling under a tap or in an ice bath will bring down the precipitate. Aliphatic derivatives as a rule respond to shaking; aromatic compounds require cooling in an ice bath.

The crude derivative is filtered, washed with 50 per cent alcoho and recrystallized from dilute alcohol in the usual manner. Because reduction in the case of aromatic nitriles is less smooth, an initial sample of 2 cc. or 2 grams is recommended.

In Table I are given the results obtained with ten aliphatic and four aromatic nitriles. The product was in most cases recrystallized from dilute alcohol, two recrystallizations usually being sufficient to yield a pure product. The method is applicable only to those aliphatic nitriles which form a volatile amine upon reduction. In the aromatic series the method works less well, probably because of the lack of volatility of the amine and the fact that reduction in the aromatic series is accompanied by side reactions.

	DIE I	IDENT	ENTERATION OF NUMBER OF			
IA	Weight of Nitrile Used	No. of Crys- talliza- tions	M. P. of Phenyl Thio- urea ° C.	Weight of Deriva- tive Ob- tained Gram	Nitrog Calculated %	en Found %
Acetonitrile Propionitrile n-Butyronitrile Isobutyronitrile Isocapronitrile Isocapronitrile Glutaronitrile ^a Succinonitrile ^a p-Tolunitrile ^a β-Naphthonitrile ^a β Naphthonitrile ^a	0.8 0.8 0.8 0.8 0.8 0.8 0.8 0.8 0.8 0.8	2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	106 63 65 69 102 77 112 148 168 168 147 144 179 140 cribed	0.8 0.7 0.6 0.7 0.6 0.3 0.25 0.9 0.9 0.3 0.10 0.3 0.33	 11.85 15.04 15.63 11.56 10.93 10.93 10.93 9.58	 11.97 15.00 15.64 11.62 10.84 11.35 9.69 could be
obtained with α -naphthonitrile or with <i>m</i> -tolunitrile.						

Literature Cited

(1) Condo, Hinkel, Fassero, and Shriner, J. Am. Chem. Soc., 59, 230

- (1937). (2) Howells and Little, Ibid., 54, 2451 (1932).
- (3) Shriner and Turner, Ibid., 52, 1267 (1930).