

TABLE I
CRYSTALLINE FORMS OF XYLITOL

Form	Metastable	Stable
M. p., °C.	61-61.5	93-94.5
α	1.519	1.549
γ	1.548	1.566
β	1.521	1.551
Crystal system	Monoclinic	Rhombic
Axial angle and dispersion	$2V = 32 \pm 5^\circ$ ($r > v$) weak	$2V = 38 \pm 5^\circ$ ($r < v$) weak
Optical character	(+)	(+)

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Suggested Method for Replaceable Hydrogen

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Dilute sodium amalgams react rapidly neither with acetonitrile nor with water dissolved therein at low concentrations. If silicon tetrachloride is added, however, the amalgam will, upon violent shaking, rapidly liberate hydrogen derived from the water initially present. Unfortunately, the reaction is not quantitative even under conditions chosen after considerable experimentation: the hydrogen is liberated in amounts ranging from one to two gram atoms for each mole of water.

Samples of known water (or alcohol) content were prepared with acetonitrile that had been distilled from phosphorus pentoxide; the solvent gave a negligible blank. 50 cc. of such a sample was measured into a 100-cc. acetylation flask attached to a mercury-filled gas buret. Ten drops of freshly distilled silicon tetrachloride was added with a dropper and dissolved by shaking the closed flask; 10 cc. of sodium amalgam (about 0.05% by weight) was now poured in, and the closed flask shaken violently for three ten-second periods; a gas buret reading was taken after each period had elapsed, the final reading being taken when temperature equilibrium had been re-established. At water concentrations below 0.05% by weight, more hydrogen could not be liberated by this procedure when amalgam or silicon tetrachloride was subsequently added. At the higher concentrations, these substances had to be added alternately in the amounts given above until no more hydrogen was evolved. Some of the results obtained are given in Table I; here all percentages are by weight, and water is assumed to have two replaceable hydrogens.

Two samples of acetonitrile in which 0.013 and 0.07% water had been obtained with the Karl Fischer reagent by Mr. Stanley Mills, Niacet Chemical Company, gave only 0.003 and 0.02% by the present method when the results were calculated as in the last column of the table. (An empirical correction would, of course, improve the agreement.) Whether the Karl Fischer reagent reacted with substances other than water in these samples is not known.

TABLE I
REPLACEABLE HYDROGEN IN ACETONITRILE SOLUTIONS

No.	Solute	% Solute added	% Solute found
1	Water	0.008	0.004
2	Water	.015	.010
3	Water	.030	.019
4	Water	.045	.031
5	Water	.060	.045
6	Water	.075	.055
7	Water	.13	.08
8	Water	.13	.08
9	Water	.13	.12
10	Ethyl alcohol	.13	.17
11	Ethyl alcohol	.13	.17
12	Methyl alcohol	.13	.12

The method suggested here is subject to complications. Silicon tetrachloride and sodium amalgam are both consumed in side reactions. Table I shows that the stoichiometry is not simple; water gives lower results than the alcohols, but this is not surprising because water (or an —OH group) is the more likely to be retained in an inactive condition by the reaction products. The amalgam becomes covered almost instantly by a film, presumably siliceous, that bars it from reacting when its surface is at rest; this simplifies the manipulation. Sodium amalgam can be slowly oxidized by the air in the system; the occurrence of this reaction, the rate of which is usually negligible, can be turned to account as a signal that the hydrogen chloride has been consumed with amalgam still present.

In spite of these complications, the proposed method may find its place where other methods are inapplicable or too slow. No doubt other substances that react like silicon tetrachloride could be used. One experiment showed that dioxane could replace acetonitrile.

The method grew out of experiments being carried on here by Dr. C. E. Reed. I am grateful also to Dr. R. O. Sauer for supplying the silicon tetrachloride, and to Mr. L. B. Bronk for helping with the determinations.

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The Preparation of β -Primeverose Heptaacetate and β -Vicianose Heptaacetate

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Recently in this Laboratory we have had occasion to prepare primeverose and vicianose in con-

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