469. *The Determination of Water in Pyridine Homologues by the Use of Infra-red Spectroscopy.*

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Published methods for the determination of water in pyridine homologues are reviewed briefly. An infra-red spectroscopic procedure is given which allows water concentrations down to 0·002% v/v to be determined rapidly and requires only 0·1 ml. of the base. A drying technique suitable for use in the measurement of the true zero absorption of these bases in the absence of water is described.

During the preparation of highly purified samples of the bases, pyridine, α-, β-, and γ-picoline, and 2 : 6-lutidine, it was realised that water was likely to be the major residual impurity. The ratio of the molecular weights of water to base are roughly 1 : 5 for this series of compounds so that 0·02% v/v of water corresponds to 0·1 mol. per cent. of impurity, and the presence of a small amount of water on a volume basis is of considerable importance when purities are expressed as a molar percentage.

" AnalaR Standards for Laboratory Chemicals," 2nd Edn., London, 1927, describes an acceptance test for pyridine founded on the presence or absence of cloudiness when 5 ml. of the base are mixed with 5 ml. of carbon disulphide. We find that pyridine containing as much as 6% by volume of water can be mixed with an equal volume of carbon disulphide and no cloudiness due to the separation of water is apparent. But on the other hand, if a sample of pyridine containing no more than 1% of water by volume is admixed with twice its volume of carbon disulphide cloudiness readily appears. With pyridine containing less than 0·25% of water a cloudiness cannot be produced, no matter in what ratio the volumes of sample and carbon disulphide are mixed.

A method which depends on the titration of the acid produced when acetic anhydride reacts with pyridine has been described by Pesez (*Ann. Pharm. franç.*, 1946, **4**, 98), but this requires

5 ml. of pyridine and is only suitable for solutions containing more than a few tenths per cent of water.

The Karl Fischer reagent (see " Aquametry " Mitchell and Smith, Interscience Publishers, New York, 1948, for a summary) can be used for determining fairly small concentrations of water, but the large quantities of pyridine required (of the order of 100 ml.) when the water content is low makes the method not so convenient as that to be described, while in this laboratory percentages of water less than 0·01% have been found to be difficult to determine with this reagent.

The method described here is based upon the qualitative observations of Bosschieter, Errera, and Gaspart (*Physica*, 1938, **5**, 115) that the height of the absorption band near 3450 cm.$^{-1}$ in the infra-red spectrum of pyridine depends upon the water concentration. The published curves show a small band in the spectrum of pyridine and in the spectra of mixtures containing 1, 6, and 12% of water. The authors attribute the band to the formation of a hydrogen bridge between the nitrogen atom of the pyridine and the water molecule.

In view of the difficulty we have experienced in obtaining and maintaining pyridine in a dry state it was decided to prepare a new specimen in order to confirm that pyridine itself has an absorption band near 3450 cm.$^{-1}$. We found this band at 3420 cm.$^{-1}$, and the measured absorption of a dry specimen at this wave number was used as the true zero absorption; water was then added in known amounts and the dependence of the height of the absorption band on water concentration established. The experiments were extended to the picolines and 2 : 6-lutidine, and it was found that 0·002% v/v of water was detectable in all these bases and that this figure also represented the uncertainty in the determined water content up to 0·05% water, when a cell 1-mm. thick was used.

EXPERIMENTAL.

The base samples employed have been prepared at the Chemical Research Laboratory and details of the preparation will be described in another paper. For the present purposes it suffices to state that no absorption bands other than that of the base under study, and water if present, were detectable.

All spectroscopic measurements were carried out on a Hilger D.209 double-beam infra-red spectrometer a rocksalt prism being used. For a description of the instrument and a discussion of the accuracy of the wave-number calibration (±15 cm.$^{-1}$ in the range 5000—2000 cm.$^{-1}$ (see Hales, *J. Sci. Instr.*, 1949, **26**, 359). The transmission of the cells used was determined with carbon tetrachloride which has a high transmission at 3420 cm.$^{-1}$.

The efficacy of various drying techniques was followed by measuring the absorption band at 3420 cm.$^{-1}$. Müller (*Sitzungsber. Akad. Wiss. Wien*, 1922, **131**, 19) has described a drying method based on electrolysis between platinum electrodes, but this was found to be very slow with pyridine with the result that, unless very special precautions were taken, water was picked up more quickly than it was removed.

Several amalgams were tried as drying agents but the main disadvantage of most of these was the slowness of the reaction. Solid sodium amalgam was found to remove water fairly rapidly but the well-known chemical reaction of sodium with pyridine quickly produced a coloration of the liquid and the appearance of a broad absorption band almost coincident with the water association band.

Distillation of a sample of pyridine containing 0·25% v/v of water from baryta had no effect on the water content.

Fractional freezing proved to be effective for the removal of water from β-picoline (m. p. −18°) although the water content could not be reduced below 0·02% v/v, as subsequently measured by the technique described below. The water content of pyridine was not reduced below 0·05% v/v by fractional freezing, probably as a consequence of the difficulty of manipulating this dry base sample at low temperatures.

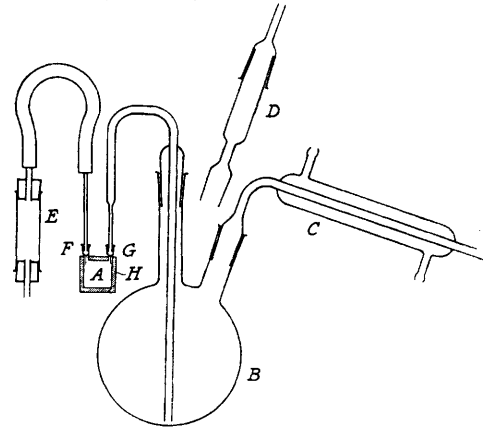
Azeotropic distillation of pyridine with benzene has been recommended as a method of reducing the water content below 0·01% (see " Aquametry," p. 67). In our experience it is difficult to remove traces of benzene from the pyridine by this procedure without the use of an efficient fractionating column, whilst if a good column is used the rate of distillation is so slow that recontamination of the pyridine with water presents a real hazard.

Pyridine forms a minimum-boiling azeotrope with water, and this may be used to dry a base sample by straight distillation without the addition of an entrainer. It was found that during the transference of dried pyridine to the spectrometer absorption cell by means of a pen-filler type of pipette water was picked up from the atmosphere to an extent corresponding approximately to 0·02% v/v. The apparatus shown in Fig. 1 was therefore constructed in order that the absorption cell (1 mm. thick) could be filled directly from the distillation flask. The dimensions of the apparatus were such that the whole equipment could be accommodated within the spectrometer.

In all the examples described below, initially approximately 300 ml. of the pyridine homologue were taken and were distilled into a graduated cylinder through *C* whilst a slow stream of dry air was passed *via* the phosphoric oxide tube *E* and through the liquid in *B*. This air current prevented the base from entering the absorption cell *A*, assisted boiling in *B*, and prevented the diffusion of atmospheric moisture into *B* through *C*. When it was decided to make a spectral measurement the distillation was discontinued, the condenser *C* was disconnected, and the joint immediately stoppered with the phosphoric oxide tube *D*, after which the current of dried air was turned off. Suction was applied through *E*, the liquid drawn over into *A* from the flask *B*, and a spectral measurement made. The cell was emptied and refilled for a second spectral measurement by applying suction through *D* and *E*, respectively. The cell *A* was flushed with liquid before filling it for each spectral determination.

FIG. 1.

Apparatus for drying of bases.



A.	*Absorption cell.*	*D*, *E*.	P_2O_5 *tubes.*
B.	*Distillation flask.*	*F*, *G*.	*Hypodermic needles.*
C.	*Condenser.*	*H*.	*Lead spacing washer.*

FIG. 2.

Drying of pyridine.

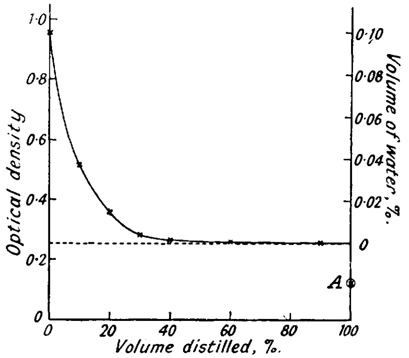
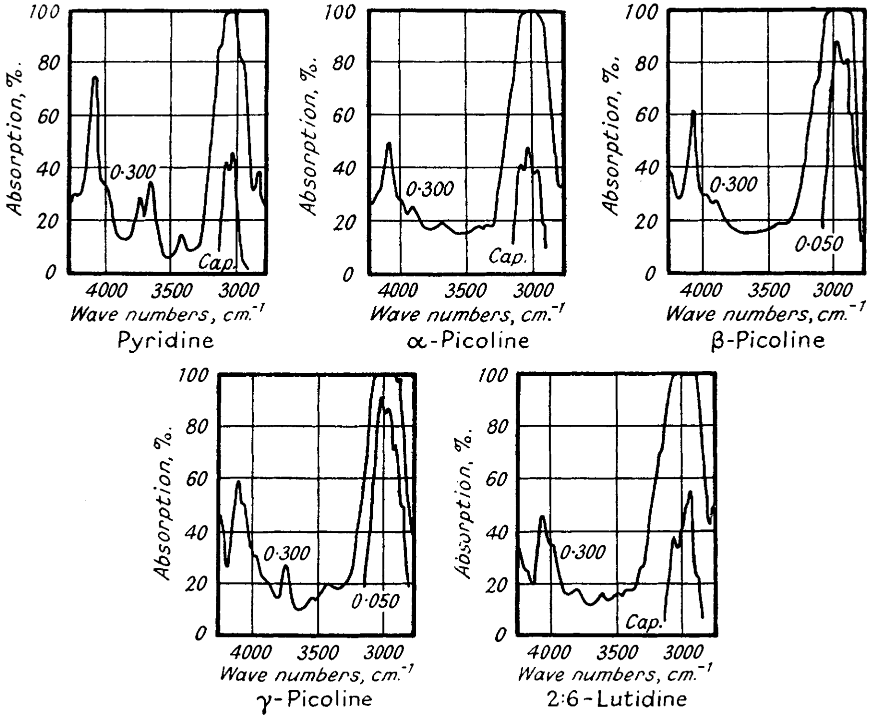


FIG. 3.

Spectra of bases in region of 3420 *cm.*$^{-1}$.



Pyridine α-Picoline β-Picoline

γ-Picoline 2:6-Lutidine

0·300, 0·050 = *cell thickness* (*mm.*). *Cap.* = *capillary*. *Spectral slit width* = 20 *cm.*$^{-1}$.

The optical density (1-mm. cell) at 3420 cm.$^{-1}$ is plotted in Fig. 2 against the volume percentage of pyridine distilled. As expected from a consideration of the relative boiling points of the azeotrope and pyridine, and of the Rayleigh distillation equation, the optical-density curve approaches an asymptotic value quite rapidly. Clearly, completely dry pyridine has some absorption near 3420 cm.$^{-1}$ and as can be seen from Fig. 3 this base itself exhibits a weak band at this wave-length.

The higher-boiling bases are more easily dried by the distillation technique than is pyridine, as can be seen from Table I; the spectra of the dry bases in the region 3000—4000 cm.$^{-1}$ are given in Fig. 3. All the bases show some absorption in this region but only pyridine has a well-marked absorption band.

By the addition of known amounts of water it was shown that the optical density varied linearly with the volume percentage of water for each base up to a water concentration of at least 0·2% v/v. A 0·300-mm. absorption cell was found to be convenient for the estimation of water in the range 0·005—0·20% *v/v*. Table II summarises the results for (*a*) optical density of the dry base, and (*b*) the change in optical density produced by 0·1% v/v of water, each expressed in terms of a 1-mm. cell. The optical density is defined as equal to [—log (percentage transmission/100)] or alternatively as [—log{1 — (percentage absorption/100)}].

The use of these values to estimate the water content of a base sample may be illustrated by data on the spectrum of a purified sample of α-picoline (purity 99·8 mol. %) published by Freiser and Glowacki (*J. Amer. Chem. Soc.*, 1948, **70**, 2575) and recently issued as spectrum No. 743 by the American Petroleum Institute Research Project 44. These published spectra show an absorption band at 3420 cm.$^{-1}$ corresponding to a percentage transmission of 86·5% in a cell 0·08 mm. thick. This corresponds to an optical density of 0·0630, and is equivalent to an optical density of 0·787 for a 1 mm. cell. Thus from Table II the volume percentage of water in this sample is 0·1(0·787 — 0·293)/0·664 = 0·07% v/v. This estimate is only approximate because there may be differences between the spectrometers and in technique.

TABLE I.

	Pyridine.	α-Picoline.	β-Picoline.	γ-Picoline.	2 : 6-Lutidine.
Water content before distillation, % v/v	0·1	0·3	3·0	0·3	1·5
Vol. fraction distilled when optical density became constant	0·9	0·5	0·5	0·3	0·3

TABLE II.

	Pyridine.	α-Picoline.	β-Picoline.	γ-Picoline.	2 : 6-Lutidine.
Optical density of dry base in 1-mm. cell	0·253	0·293	0·285	0·329	0·275
Change in optical density produced by 0·1% v/v of water	0·700	0·664	0·612	0·670	0·671

This volume percentage corresponds to a mol. percentage of 0·41 of water, which is rather greater than the total impurity reported (0·24 mol. %), but unless special precautions were taken during filling of the absorption cell this quantity of water could easily have been absorbed during transference—indeed concentrations of less than 0·02% v/v are very difficult to determine unless the pyridine can be transferred to the absorption cell in a closed system.

Larger quantities of water can be determined either by using a thinner cell with the appropriate calibration curve or by diluting the specimen with dry base to bring the water content within the range covered by Table II.

In conclusion it is of interest to note that the band at 3420 cm.$^{-1}$ is only present when pyridine and water are in the liquid phase for we have found that 3% of water by volume with pyridine in the vapour phase produces no detectable difference in the absorption spectrum at 3420 cm.$^{-1}$ although pyridine vapour itself shows little absorption at this wave-length.

The work described has been carried out as part of the research programme of the Chemistry Research Board and this paper is published by permission of the Director, Chemical Research Laboratory, Teddington.

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[*Received, April* 16*th*, 1951.]