

The Ultraviolet Light Absorption of Ethyl Alcohol Purified by Different Methods.—According to Bielecki and Henri¹ the first ultraviolet absorption band of pure ethyl alcohol begins at about $\lambda 2500 \text{ \AA.}$, and extends, with increasing strength, down at least to 2100 \AA. On the other hand, many of the impurities ordinarily found in ethyl alcohol (*e. g.*, aldehydes, resins, etc.), shows strong absorption bands at longer wave lengths. It follows that measurements of the absorption coefficients of ethyl alcohol in the threshold region, $\lambda 2500\text{--}3000 \text{ \AA.}$, should provide a very delicate method for the detection of impurities of this type.

We have observed a considerable variation in the absorption spectra in the threshold region of samples of ethyl alcohol purified by different methods, and believe that absorption measurements can be used to determine to some extent the efficiency of different methods of purification.

In Table I, and on Fig. 1, are compared the absorption coefficients of samples of ethyl alcohol which have been subjected to the following treatments. All distillations were made through a fractionating column, only the center portion of the distillate being collected in each case.

A. Stock 95% ethyl alcohol, without purification.

B. Alcohol "A" was dried over calcium oxide, then 1 g. of iodine added per liter of alcohol. The solution was allowed to stand for several days and then distilled. To this was added 1 g. per liter of pure powdered zinc, the mixture being refluxed for several hours and again distilled.²

C. To alcohol "A" was added, per liter, 25 cc. of 12 *N* sulfuric acid. The mixture was refluxed for several hours and distilled.

D. The product from "C" was treated with 20 g. of potassium hydroxide and 10 g. of silver nitrate per liter, the mixture being refluxed and distilled.

E. Alcohol "D" was allowed to stand for one week over specially prepared pure calcium oxide, then distilled slowly on a water-bath.

F. Treatment same as in "E" except that the solid matter (calcium oxide and hydroxide) was filtered off before distillation.

G. Same as "E" except that the whole process, from first addition of calcium oxide, was carried out in an atmosphere of pure nitrogen.

H. Alcohol "D" was allowed to stand for one week over active aluminum amalgam, filtered and distilled.

The absorption measurements show clearly that the treatment of stock alcohol with dilute sulfuric acid, followed by distillation, produces a tremendous improvement in purity (curve C). Another marked improvement is produced by the treatment with alkaline silver oxide (curve D). This is no doubt due principally to the removal of aldehydes.

If the next step be distillation in air from calcium oxide, after standing, in the usual manner, a very pronounced increase in absorption is observed (curve E), indicating the formation of some absorbing impurity. Upon filtering off the calcium oxide before distillation, a less marked

¹ Bielecki and Henri, *Ber.*, **45**, 2819 (1912); *Compt. rend.*, **155**, 456 (1912).

² Castille and Henri, *Bull. soc. chim. biol.*, **6**, 299 (1924).

TABLE I
ABSORPTION COEFFICIENTS

λ	$k \times 10^3$								
	A Stock 95%	B I ₂ + Zn method	C H ₂ SO ₄ + H ₂ O distillation	D "C" + Ag ₂ O	E "D" + CaO distillation	F "D" + CaO filtered	G "D" + CaO in N ₂	H "D" + Al amal.	I Henri values
3710	2.8					
3500	8.2					
3320	13.0		1.1		2.9				
3160	18.1		1.9		3.1				
3020	25.1		2.9	...	9.7				
2890	34.8	0.5	3.1	0.02	10.2	...	0.15	..	
2780	50.4	2.0	5.1	.4	13.7	1.7	.43	0.30	..
2675	77.5	3.8	5.5	.5	15.1	3.1	.65	.45	..
2585	..	6.0	6.7	.9	17.6	4.5	1.2	.58	4.0
2500		8.8	9.6	2.0	20.3	6.4	2.2	1.33	6.2
2430		12.4	14.5	3.3	24.8	9.7	3.5	2.85	10.0

increase in absorption is obtained (curve F), and upon keeping the alcohol in an atmosphere of nitrogen during the entire treatment and distillation, no change in absorption is observed (curve G).

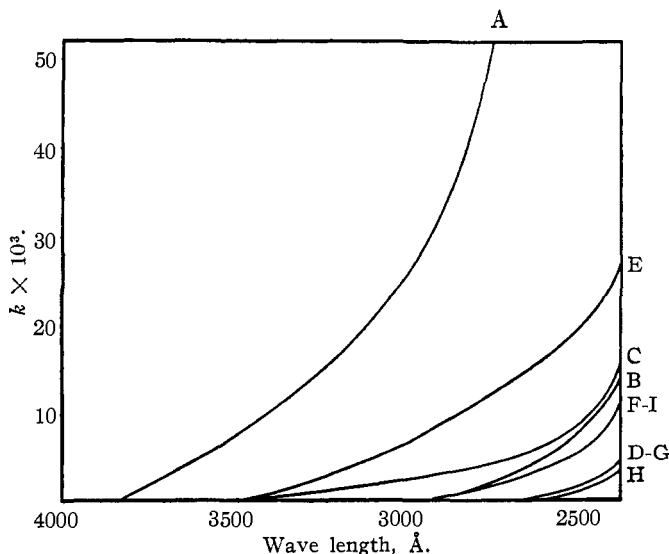


Fig. 1.—Absorption coefficients for various alcohol samples.

This suggests that the alcohol is oxidized by calcium oxide in the presence of air, the reaction proceeding very slowly at room temperature, and much more rapidly during distillation. The oxidation does not occur in the absence of oxygen, and hence the drying of ethyl alcohol over calcium oxide should be carried out in nitrogen.

Drying over aluminum amalgam gives the lowest absorbing, and hence

the purest alcohol of any of the methods used here. It should be pointed out, however, that non-absorbing impurities, such as water, are not detected by absorption measurements. The electrical conductivity may be used to detect the presence of small amounts of water, and a comparison of the conductivities of the different samples indicated that aluminum amalgam is fully as efficient a drying agent as calcium oxide. Metallic calcium, used as a drying agent, failed to give any better results than calcium oxide, either for light absorption or conductivity.

The iodine-zinc method of purification (curve B) does not give quite as good results as the other methods.

It is of interest that the absorption measurements of Bielecki and Henri (column I) which are the lowest hitherto reported, agree almost exactly with our alcohol F, while our samples D, G and H show a lower absorption in this threshold region.

In short wave lengths, however, where alcohol itself absorbs strongly, one would expect the difference between the various samples to be slight.

Summarizing, light absorption measurements indicate that the standard practice of drying ethyl alcohol over calcium oxide should be carried out in an oxygen-free atmosphere. The highest degree of purity, as measured by the absorption spectrum, is obtained by the use of aluminum amalgam for drying.

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SOME FACTORS AFFECTING THE CATALYTIC ACTIVITY OF COBALT OLEATE IN THE AUTOXIDATION OF PENTENE-2¹

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(A) Introduction

In a paper published some months ago,² the authors noted the catalytic activity of certain substances on the autoxidation of cracked gasolines. It was ascertained at that time that hydrogen chloride, for example, was a strong autoxidizing catalyst, whereas acetic acid was almost without effect. These reactions, as well as numerous other indications, prompted the authors^{2,3} to propose a new theory of autoxidation based on the acidic

¹ Presented before the Petroleum Division of the American Chemical Society at Cincinnati, Ohio, September 9-13, 1930.

² Wagner and Hyman, 10th Annual Meeting, A. P. I. Report, 3rd section, pages 118-123.

³ Hyman and Wagner, *J. Inst. Pet. Tech.*, **15**, 645 (1929).