The Preparation of Absolute Ethyl Alcohol.—By E Gordon Young, Ph.D., Department of Biochemistry, Dalhousie University, Halifax, N. S.

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Abstract.

A comparative study has been made with reference to percentage yield and cost per litre of product of three methods of preparing absolute alcohol for ordinary chemical procedures and for histological work. These comprise: (1) the carbide method, (2) fractional distillation with benzene, (3) the lime method. It is concluded

(1) That the carbide method produces the best yield (95%) at a cost slightly higher than the lime method but of a product from which it is difficult to remove traces of impurities of objectionable odour, if ordinary carbide is used. This is the most rapid procedure.

(2) That the method of benzene distillation is impracticable on a laboratory scale.

(3) That the lime method is the cheapest with a yield of about 80%. It is recommended in the proportion of 300 gms. of fresh lime to 1 litre of 95% alcohol, refluxed for about four hours and distilled.

Methods for the preparation of absolute ethyl alcohol are very numerous (MacArdle,[1]). Few of them, however, are well suited to the production of large quantities on a laboratory scale. For economic reasons it became necessary to prepare absolute alcohol of a grade of 99.6% or slightly better in half gallon quantities, frequently, at as low a cost as possible. This product was to serve for the dehydration of histological sections, both plant and animal, and also for a variety of organic chemical work not requiring any high degree of purity as regards water content. In the course of some three or four years experience records have accumulated in the comparison of costs and optimal conditions for several methods. For the reason that our problem has undoubtedly arisen in many laboratories, yet the literature contains so few articles bearing on the economic production of absolute alcohol in the laboratory as contrasted with its commercial preparation, a brief report of our results has been deemed advisable.

1. MacArdle, *Solvents in Synthetic Organic Chemistry*, D. Van Nostrand Co., New York, pp. 51-73, (1925).

The methods selected for trial were (1) the calcium carbide process, (2) fractional distillation with benzene, (3) the unslaked lime process. Our results have shown that although much the best yields are obtained with carbide the lime procedure is the most economical under the conditions developed. The benzene method, despite its general commercial use, is not applicable in the laboratory, unless possibly very large quantities are required. We have had no experience with the glycerol method.

In computing costs no account has been taken of the time of the attendant, nor of the coal gas consumed. A laboratory assistant usually carried out the operations in spare time. The cost of the original ethyl alcohol, 65 o. p., (95.0%) laid down in Halifax, N. S., was between $2.45 and $2.77 per Imperial gallon.

Experimental.

The Carbide Method.—There are few references in the literature to the use of calcium carbide for dehydrating alcohol. It was first suggested by Yvon[2] in the proportion of 25 gms. of carbide to 100 gms. alcohol, 90-95%, followed by a second distillation in the presence of anhydrous copper sulphate. The method was applied to the preparation of absolute methyl alcohol by Cook and Haines[3]. Lyons and Smith[4] revived the method in 1925 using 17.5 gms. of carbide of 20 mesh size and 81% purity. They refluxed the mixture for 30 minutes and recommended the addition of anhydrous $CuSO_4$ to remove acetylene as did Yvon. Their yield was 98.7% and the grade of dehydration 99.86% by volume.

We have followed the general procedure of Lyons and Smith but have found it necessary to use a proportion of 25 gms. of coarsely powdered commercial carbide to 100 gms. of 95% alcohol. This mixture was refluxed for two hours; then 1 gm. anhydrous $CuSO_4$ was added per 100 gms. alcohol and refluxing continued for one hour. The product was then distilled and assayed 99.7% by volume with a specific gravity

2. Yvon, *Compt. rend.*, **125**, 1181, (1897).
3. Cook and Haines, *Proc. Iowa Acad. Sci.*, **9**, 86, (1901).
4. Lyons and Smith, *Science*, **62**, 224 (1925).

of 0.796. This material however frequently possessed a marked odour despite the copper treatment. A second treatment with anhydrous $CuSO_4$ in the proportion of 1-2 gms. per 100 gms. followed by distillation usually removed the odour but decreased the yield to 95% of theoretical. The cost per litre of absolute over the preparation of an Imperial gallon became $1.34; in the best run it was $0.89. This is calculated on the basis of 1 lb. carbide at $0.20 and 1 lb. $CuSO_4$ $1.15.

The Benzene Method.—The procedure of Young[5] was followed in detail using a fractionating column of 22 bulbs. The results of one experiment will illustrate the difficulty of applying this method to small scale operations. 2000 c.c. alcohol and 1500 c.c. benzene were mixed and fractionated into the usual four fractions separating as follows:

(1) ternary mixture, 64.8-67.5°—2000 c.c.
(2) binary mixture, 67.5-73.0°—375 c.c.
(3) binary mixture, 73.0-78.3°—800 c.c.
(4) absolute alcohol, 78.3°—300 c.c.

Without doubt too much benzene was used initially. The time required for efficient separation coupled with the small yield obtained make this method impossible on a laboratory scale. The details of recovery of the benzene and refractionation of the various mixtures are omitted.

The Lime Method.—The procedure in vogue at different laboratories varies greatly in carrying out dehydration of alcohol with unslakedl ime. In 1907 Kailan[6] published a paper in which two variables, ratio of lime to alcohol and time of contact, were investigated. His conclusions as regards the first were that no difference in the rate of dehydration was apparent between 250 and 410 gms. of lime per litre of alcohol and that above 400 gms. the rate increased rapidly. The yield of alcohol was however decreased proportionally. Adopting 550 gms. per litre as a

5. Young, *J. Chem. Soc.*, **81**, 707, (1902).
6. Kailan, *Monatsh.* **28**, 927, (1907).

good proportion Kailan found that three and a half hours' refluxing produced a grade of 99.5% while six hours increased the dehydration to 99.9%. The same result could be attained by standing at room temperature for twenty-four days. Ln 1910 Warren[7] published the description of a copper still for making absolute alcohol by the lime method. He claimed that 99.87% was the best possible grade obtainable by this process. He refluxed for six hours with a large excess of lime but does not state the exact amount. Twenty-four hours' standing in contact with lime at room temperature saved one hour in refluxing. His yield was approximately 70% of theoretical. Wightman, Wiesel and Jones,[8] prepared a sample, 99.964%, sp. gr. 0.785067, for conductivity purposes by boiling with lime for several days. Dannar and Hildebrand[9] in preparing absolute alcohol for the same purpose used a proportion of 600-700 gms. per litre of 95% and refluxed eight hours, besides purifying it in other ways. Finally Noyes[10] in 1923 published the results of preparing large quantities of absolute for special work in his laboratories using a proportion of 250 gms. of lime per litre of 95% grade and refluxed on a steam cone overnight; then distilled to yield a grade of 99.6-99.7%. There was a loss of 7-8% despite a prolonged heating of the lime residue. A fresh treatment of this grade in the proportion of 40 gms. powdered lime per litre produced 99.9% absolute. Lassar-Cohn[11] favors the old method used by Squibb[12] of prolonged treatment with lime in the cold, requiring eight to fourteen days. There is thus in the literature divided opinion as to time of contact (from 3½ hours to 14 days), as to proportion of lime (from 250 gms. to 700 gms. per litre of 95%), and as to the temperature employed.

Our practice has been to start the individual preparations listed below with three litres of 95.0% by volume in a 5 litre

7. Warren, *J. Am. Chem. Soc.*, **32**, 698, (1910).
8. Wightman, Wiesel, and Jones, *J. Am. Chem. Soc.*, **36**, 2243, (1914).
9. Dannar and Hildebrand, *J. Am. Chem. Soc.*, **44**, 2826. (1922).
10. Noyes, *J. Am. Chem. Soc.*, **45**, 859 (1923).
11. Lassar-Cohn, *Organic Laboratory Methods*, Trans. from the 5th. German Ed., by R. E. Oesper, Williams & Wilkins, Baltimore pp. 394-395, (1928).
12. Squibb, *Z. anal. Chem.*, **26**, 94, (1887).

pyrex flask on a sand bath using a 24 inch condenser. In refluxing we have found the use of a trap containing a few cubic centimeters of alcohol increases our yield. In collecting the absolute during distillation from the lime residue the product is protected from the air by a calcium chloride tube in the receiver. This we have found a necessary precaution because of the absorption of water from the air during the course of the distillation. Winkler[13] claims the absorption of 0.1% in 15 minutes; Crismer[14] 0.2% in 25 minutes, and 0.7% in 90 minutes. We have found our preparations, at first negative to the $KMnO_4$ and CaC_2 tests, passing over the absolute line of 99.5% and becoming positive to these tests in a few hours. The specific gravities were determined by accurate spindles at 15°C. and converted to percentage by volume figures from standard tables.

Our first few runs demonstrated the importance of the use of *fresh* unslaked lime in obtaining a good yield of absolute quality. The procedure in Table 1 was to allow the lime to remain in contact with the alcohol for 24 hours at room temperature, then to reflux three hours and distil.

TABLE 1.

Alcohol c.c.	Lime gms.	Yield c.c.	Concentration %	$KMnO_4$ Test.
1000	450	600	99.5	+
1000	350	730	99.2	+
1000	300 (fresh)	700	99.7	—
1000	250 (fresh)	730	99.2	+

The theoretical amount of lime required to dehydrate completely one litre of 95% alcohol is 155 gms. (CaO).

From several experiments done with and without the procedure of preliminary standing using the same quantity of lime it was proven that early contact in the cold could be neglected as it did not alter either yield or the time of refluxing materially. Furthermore an accumulation of finely divided lime on the bottom of the flask increased the danger of cracking

13 Winkler, *Ber.*, **38**, 3612, (1905).
14. Crismer, *Bull. Soc. Chim. Belg.*, **18**, 18, (1904).

the flask on subsequent heating. The yield of absolute alcohol depends upon the ratio of lime to alcohol, and upon the time of heating of the lime residue. The former is apparent from the following table in which all runs were simply refluxed for $2\frac{1}{2}$ hours, then distilled.

TABLE 2.

Alcohol c.c.	Lime gms.	Yield c.c.	Concentration %
1000	200	785	98.3
1000	300	730	98.8
1000	400	670	99.1
1000	500	580	99.5

The concentration of alcohol is thus shown to be directly proportional to the amount of lime used as one would expect. The yield is however inversely proportional, if the same care is taken in baking the lime residue until practically no further distillate is obtainable. This is an important factor in yield and consequently in cost. Yields may vary tremendously if the latter part of the distillation is not prolonged. This is shown in Table 3. We have always found under our conditions of heating that the last few cubic centimeters of distillate are as good, if not better in quality, than the whole. Furthermore an adequate amount of baking causing the lime mass to dry and crack forms a residue which can be shaken into small lumps and removed from the flask without difficulty.

TABLE 3.

Alcohol c.c.	Lime gms.	Yield c.c.	Concentration %
1000	300	670	99.7
1000	300	570	99.7
1000	250	580	98.8
1000	300	730	99.2
1000	300	600	99.4

The factor of time of refluxing was next considered in relation to the practicability of the preparations being complete in the course of a day. Table 4 illustrates several distillations with this end in view.

TABLE 4.

Alcohol c.c.	Lime gms.	Yield c.c.	Time of Refluxing hrs.	Concentration %
1000	300	730	2.5	98.8
1000	300	725	4	99.7
1000	300	720	5	99.9
1000	300	740	7	99.9
1000	200	760	6	99.2

It would be supposed, *a priori*, that if the lime were in a finely powdered state rather than in coarse lumps the rate of dehydration would be considerably accelerated. A single comparative experiment was done to test this. Two lots of alcoho lwere treated with 300 gms. of lime each, one finely powdered and the other coarse lump. They were allowed to stand at room temperature for 24 hours, refluxed for 2½ hours, then distilled. The yield from the finely powdered lime was 570 c.c. per litre of 98.8% grade, from the lump, 700 c.c. per litre of 99.4%. There is thus a disadvantage in using powdered lime, as neither the yield nor the grade is quite as good. Probably in the process of powdering the lime a certain amount of moisture is absorbed which decreases its efficiency. Furthermore the manual labor involved is very tedious. Finally there is increased danger of caking during heating with the possibility of cracking a glass container with resultant fire. The lumps break up quickly after boiling sets in so that over a period of several hours any advantage that the powder may have in theory is lost.

Cost of Production. The yield of alcohol under optimal conditions outlined above is about 78%. The low cost of alcohol and of lime however compensates for the low yield. Allowing lime at our purchase price of $1.00 for 50 lbs., and alcohol at $2.50 per Imperial gallon, the cost per litre of absolute becomes $0.89. This is very favourable as compared with $1.34 per litre as prepared by the carbide method and equal to the best experiment of this method. Furthermore the yield of absolute by the lime procedure could probably be bettered with care and practice.

It is evident from the preceding tables that different amounts of lime may be used to prepare the absolute grade since the time required for refluxing varies inversely as the amount of lime used. This is mentioned because our experiments were used to demonstrate the most economical method of producing about two litres at a distillation. If larger amounts were required it would be more economical probably to decrease the amount of lime to 200-250 gms. and increase the length of refluxing to 8-10 hours, as recommended by Noyes[10] since the preparation could not be finished in a working day.