

Table I. Experimental Determination of Total Hydration

Material	Hydrate, Gram ( $M$ )	Solvent, ml. ( $V$ )	Solvent Ratio Hydrogen to Deuterium ( $r$ )	Solution Ratio Hydrogen to Deuterium ( $R$ )	Experimental Hydration with Standard Deviation of Mean ( $f$ )	Theoretical Hydration	% Deviation, Experimental and Theoretical
CuSO <sub>4</sub> ·5H <sub>2</sub> O	0.770	1.00	0.011	0.286	0.354 ± 0.003	0.361	1.9
Na <sub>2</sub> S <sub>2</sub> O <sub>5</sub> ·5H <sub>2</sub> O	0.648	1.00	0.011	0.249	0.364 ± 0.003	0.363	0.3
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ·5H <sub>2</sub> O	0.779	1.00	0.011	0.289	0.353 ± 0.003	0.363	2.8

selected pressures between 0.1 and 1 mm. of mercury. Measurements were taken by successively scanning the hydrogen and deuterium emission lines.

#### PROCEDURE

The hydrated sample was weighed on an analytical balance. This sample was mixed with a volumetrically determined quantity of the deuterium oxide-hydrogen oxide mixture containing about 99% deuterium oxide. The solvent was separately tested to determine the exact ratio of hydrogen oxide to deuterium oxide. The sample of hydrate dissolved in solvent was then heated to accelerate the equilibrium between solvent and hydrate water. The solution then was tested to find the final ratio of hydrogen oxide to deuterium oxide.

If the molar ratio of the hydrogen oxide to deuterium oxide in the original solvent is  $r$ , and the final molar ratio of the solution is  $R$ , then the fraction by weight of the hydrated sample which is water,  $f$ , is given to a first approximation by the following relation:  $f = \frac{(R - r)V}{(1 + r)M}$ , where  $V$  is the volume of the solvent in milliliters and  $M$  is the weight of the original hydrate in grams. The approximation, which is good to about 4 parts in 1000, is introduced by assuming that the partial molar volumes of hydrogen oxide and deuterium oxide are the same, and that the density of water in the range of room temperature is 1.000. Table I presents some typical experimental results taken from a number of determinations on copper sulfate sodium thiosulfate. Each value of  $R$  and  $r$  is the mean of nine consecutive readings. The theoretical values of  $f$  are obtained from the stoichiometry of the hydrated crystals. As the purpose of this note is to describe

the basic methods, the choice of substances employed in Table I was for purposes of convenience in testing.

#### DISCUSSION

The principal error in this method was due to the pressure fluctuations in the discharge tube during the scanning which changed the values of the intensity readings. A new system is under construction which is designed to stabilize the pressure and should allow for an accuracy of better than 1%.

While the method of water analysis has been worked out for hydrated crystals, it should be applicable for determining the water content of any system which does not contain labile hydrogens. In systems containing labile hydrogens the method may be used to assay for the total concentration of these atoms. The technique is perfectly general, and applications are planned for the study of water binding and transport in biological systems.

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## Improved Permanganate Time Test for Control of Ethyl Alcohol Quality

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THE permanganate time test is well established in ethyl alcohol production and trade for indication of chemical purity (1, 2). The test, which involves reduction of permanganate, is a measure of easily oxidizable impurities, acetaldehyde, crotonaldehyde, etc., in commercial ethyl alcohol. Because of its established position in trade specifications, the test is considered of prime importance in control of ethyl alcohol quality in the Houston synthetic ethyl alcohol plant of Shell Chemical Corp. The ideal test would be one which could be conducted at the operating unit by nontechnical personnel, yielding unequivocal results in a minimum of time, and requiring simple and relatively nonfragile equipment which could be easily replaced by standard items in case of breakage.

As described by Allen (1) and used by the alcohol industry, the test has been conducted essentially as follows:

**Reducing Substances (Permanganate Test).** A glass-stoppered cylinder is thoroughly cleaned, rinsed with distilled water and then with the alcohol to be tested. Cleaning with strong hydrochloric acid to remove oxides of manganese is advisable if the cylinder has been used previously for this test. A 50-ml. portion of the alcohol to be tested is introduced, the cylinder contents are cooled to approximately 15° C., and 2 ml. of a freshly prepared potassium permanganate solution containing 0.2 gram per liter is added by means of a pipet, the exact time being noted. The contents are mixed at once by inverting the stoppered cylinder, which is then placed out of bright light and kept at 15° to

16° C., using a water bath if necessary. The number of minutes required for the complete disappearance of the pink color is the permanganate time of the alcohol.

For purpose of reference, this test can be designated as the complete fading procedure.

The end point of the complete fading procedure is difficult to determine because of the asymptotic nature of the color fading; consequently, the reproducibility of the test is poor. Two modifications of the test were suggested by Allen (1) to overcome the difficulty of judging the end point. In the first, the color of a previously reduced sample is employed as a standard to aid in determining the proper end point. This procedure also lacks precision since the color of the proposed standard fades continually during the test, and the sample and standard fail to reach an exact match. The other modification suggested involved color comparison with the Barbet standard, the salmon-colored aqueous solution prepared with a low concentration of uranium nitrate and cobaltous chloride. Since the Barbet standard is pink in color, the test time is shorter than in the complete fading procedure.

Use of the spectrophotometer as a means for improving the precision of the permanganate time test was suggested by Rask and Hildebrandt (2). Although the use of a spectrophotometer does yield results of improved precision, such an instrument was

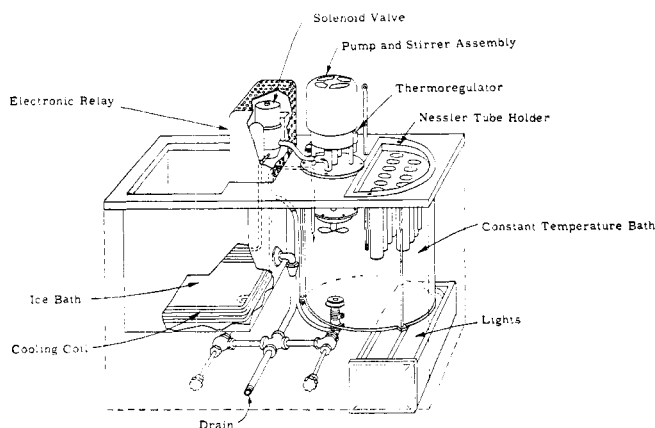


Figure 1. Schematic Diagram of Apparatus for Permanganate Time Test

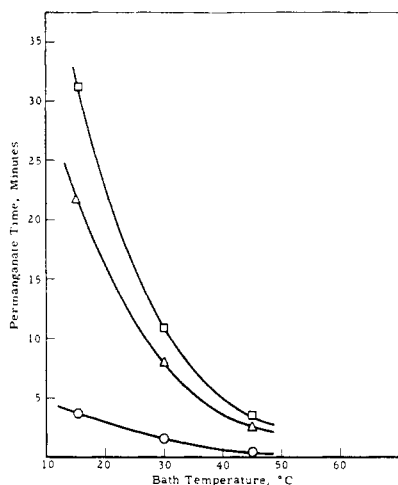


Figure 2. Influence of Temperature on Permanganate Time of Ethyl Alcohol  
Results on three synthetic pilot plant samples

Table I. Influence of Light on Permanganate Time

Lighting Conditions	Permanganate Time, Minutes
Light on continuously, no cover on top	32.5, 33
Light off, top covered during first 30 minutes of test	34, 35

considered more elaborate than desired for plant control, especially since multiple tests were required at a closely controlled temperature.

Of the possible modifications of the permanganate test suggested, a visual method based on the use of the Barbet standard appeared most promising to provide the simple test and equipment required for plant control.

#### APPARATUS

The design of the apparatus is shown in the schematic, cut-away drawing of Figure 1. The basic elements are a comparator bath consisting of a  $10\frac{1}{8} \times 10$  inch outside diameter borosilicate glass jar, with sandblasted bottom, and an ice bath containing a cooling coil. The required test temperature is maintained by pumping water, intermittently, from the comparator bath through the coil in the ice bath and then back into the comparator bath, where it is discharged near a stirrer. The pump, which operates from the same motor as the stirrer, is allowed to operate continuously. The passage of water through the cooling system is controlled by a thermoregulator actuating a solenoid valve through an electronic relay. Both the comparator bath and the ice-water reservoir are equipped with drain and overflow lines. The Nessler tube holder accommodates ten 50-

ml. low-form tubes and is so constructed that the tubes are shielded from all but the diffuse light from below. It is preferable to have the Nessler tube assembly removable to allow cleaning of the bath. The source of light is a pair of daylight-type fluorescent lamps mounted in a drawer located beneath the bath. The cooling system was found capable of reducing the temperature of the bath from room temperature ( $25^{\circ}\text{C}.$ ) to the operating temperature ( $15^{\circ}\text{C}.$ ) in approximately 40 minutes. Once the operating temperature was reached, the cooling water was required to flow only 15% of the time, the ice consumption being 5 pounds per hour. The temperature control system maintained the bath within  $\pm 0.05^{\circ}\text{C}.$

#### REAGENTS

**Cobaltous Chloride Solution.** Prepare by dissolving 50.0 grams of c.p. hexahydrate crystals in sufficient distilled water to make 1 liter of solution.

**Potassium Permanganate Solution, 0.02%.** Prepare fresh each day by dissolving  $200 \pm 1$  mg. of c.p. potassium permanganate in 1 liter of distilled water.

**Uranyl Nitrate Solution.** Prepare by dissolving 40.0 grams of c.p. hexahydrate crystals in sufficient distilled water to make 1 liter of solution.

**Alcohols for Testing.** These were pilot plant, synthetic ethyl alcohol products.

**Color Standard.** Pipet 5 ml. of the cobaltous chloride solution and 7 ml. of the uranyl nitrate solution into a cleaned 50-ml. Nessler tube. Fill to the 50-ml. mark with distilled water and mix with a stirring rod. Prepare fresh daily.

#### PROCEDURE

Clean the Nessler tubes with concentrated hydrochloric acid to remove oxides of manganese. Wash thoroughly with tap water, then rinse several times with distilled water. Place the tube containing the color standard in the water bath, regulate the bath to  $15^{\circ} \pm 0.2^{\circ}\text{C}.$ , and turn on the fluorescent lights. Rinse a cleaned Nessler tube with two 10-ml. portions of the sample to be tested, fill to the 50-ml. mark with sample, and place in the bath. Allow 15 minutes for the tube to equilibrate to bath temperature, then add 2 ml. of 0.02% potassium permanganate solution by means of a pipet, previously rinsed with a portion of the permanganate solution; note the exact time of initial addition. Mix the contents at once with a clean, dry stirring rod. Determine the time required for the sample to reach a match with the standard, comparing the sample with the standard at 30-second intervals (without removing from the bath) as the match point is approached. When testing more than one sample at a time, place suitable covers (black plastic caps for screw-cap bottles are convenient) over all Nessler tubes, except the color standard, in order to avoid interference. It is best to compare only one sample at a time with the standard. Record the time to the nearest 0.5 minute. Allow the light source to operate continuously during the test.

#### RESULTS AND DISCUSSION

**Test Variables.** The most satisfactory end point color standard was found to be that defined above, other concentrations of uranium nitrate and cobaltous chloride being found to give poorer matches than the mixture recommended. To establish the influence of light on permanganate time as determined in this equipment, two experiments were made with the light on continuously, and two with the light off and the top covered during the first 30 minutes. As shown by the data listed in Table I, it was found that light has only a slight influence on the permanganate time. Accordingly the method was written to specify that the light operate continuously during the test for reasons of convenience.

**Precision of the Test.** The precision of the proposed method was determined by analyzing a series of six pilot plant, synthetic ethyl alcohol samples, with six operators, new to the procedure, participating. The maximum range of values (Table II) obtained for each alcohol sample was found to be in the order of  $\pm 1$  minute.

To obtain a comparison of the precision of the proposed method and the complete fading procedure, the six alcohol samples listed in Table II were analyzed by the latter method, with three operators, new to this procedure, participating. The complete fading procedure was found (Table III) to have considerably poorer precision than the proposed method, the maximum range of

values being as great as 18 minutes. The comparison of the precision in Tables II and III distinctly shows the advantage of the proposed method. It is recognized that the complete fading procedure in the hands of operators of a given laboratory, experienced with the method, may give considerably better precision between operators than that indicated by Table III. However, it is also known that results from different laboratories, even when obtained by experienced operators, may show considerable deviation. One of the important advantages of the proposed method is that it eliminates operator judgment as to choice of end point color, a factor which is inherent in the complete fading procedure.

**Correlation of Permanganate Times with the Complete Fading Procedure.** To obtain a correlation factor between the two methods, the average values obtained on the six alcohol samples have been compared. The ratio of permanganate times by the two methods varied from 1.5 to 2.1, the average factor being 1.7.

**Influence of Temperature on Permanganate Time.** The influence of temperature on permanganate time for several synthetic, pilot plant alcohol samples was studied using the proposed method with bath temperatures of 15°, 30°, and 45° C. Temperature was found (Figure 2) to have a pronounced effect on reaction time. Since the effect of temperature was such that a rise of 10° C. halved the permanganate time, the range of  $\pm 0.2^\circ$  C. employed would affect the results by approximately  $\pm 2\%$ , which is within the precision found for the method.

**Influence of Blending on Permanganate Time.** Blending alcohol samples of widely differing permanganate times did not produce a linear relationship between concentration and permanganate time. On the contrary, as shown in Figure 3, a small addition of low permanganate time material was found to lower the permanganate time of the mixture markedly.

**Influence of Water Content on Permanganate Time.** The influence of water content on permanganate time was studied in the range from approximately 6 to 50% by weight of water in alcohol by experiments with an alcohol sample having a water content of 6.1% by weight, to which additional water was added. As shown in Figure 4, it was found that the permanganate time goes through

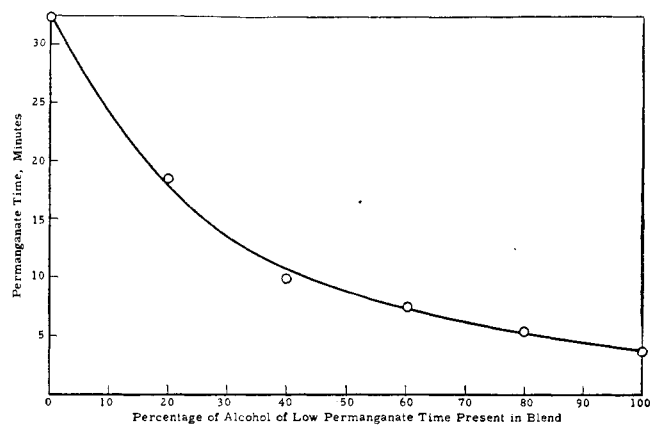


Figure 3. Influence of Blending on Permanganate Time of Ethyl Alcohol

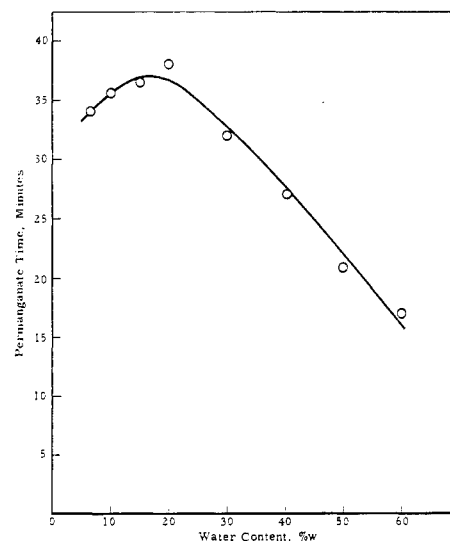


Figure 4. Influence of Water Content on Permanganate Time of Ethyl Alcohol

Table II. Precision of the Proposed Permanganate Time Test Method

Operator	Sample					
	A	B	C	D	E	F
	Permanganate Time, Minutes					
I	32.5	23	14	...	...	...
	33	22.5	14.5	...	...	...
II	32.5	22.5	12.5	3.5	22	32
	32.5	23	12.5	3.5	23	31.5
III	32.5	22.5	13	4	21	32.5
	33	22.5	13.5	4	21.5	32
IV	32.5	22.5	14	3	21.5	32
	33	23	14	3.5	21.5	31.5
V	33	23.5	14.5	4.5	22	32.5
	33.5	23.5	13.5	4	22.5	33
VI	...	...	...	4	23	34
	...	...	...	4	23	33
Average	33	23	14	4	22	32
Maximum range	1	1	2	1.5	2	2.5

Table III. Precision of the Complete Fading Procedure

Operator	Sample					
	A	B	C	D	E	F
	Permanganate Time, Minutes					
II	58	41	20	6.5	53	63
	55	48	22	6.5	49	61
IV	...	...	...	7	40	49
	...	...	...	8	39	50
V	41	31.5	21.5	...	...	...
	40	32	21.5	...	...	...
Average	49	38	21	7	45	56
Maximum range	18	16.5	2	1.5	14	14

a maximum at 20% water, the increase in time being due perhaps to a dilution effect. However, this effect is overcome by another reaction between 20 and 60%, where a steep decline in permanganate time was found. Experiments were not carried beyond 60% water content, but it was to be expected that the curve would rise beyond this point because of the high permanganate time of water.

**Influence of Storage on Permanganate Time.** No deterioration of alcohol takes place, as measured by permanganate time, on storage in brown glass bottles maintained in a dark cabinet over a period of several months. Storage in clear glass bottles, especially in locations exposed to sunlight, was found to affect the permanganate time greatly. An alcohol sample stored in clear glass and kept on a bench top near a window deteriorated from 29 to 2 minutes permanganate time in 2 months.

#### ACKNOWLEDGMENT

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