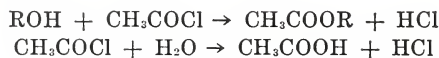


A Rapid Method for the Estimation of Alcohols

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In connection with another research problem it became necessary to estimate the quantity of methanol present. Since many samples were to be analysed, it was desirable that the method be as rapid as possible. Methods reported in the literature for the determination of alcohols are all based upon the reaction of the alcohol with acetic anhydride or acetyl chloride, followed by hydrolysis of the excess reagent, according to the following equations:



The difference in titre between a blank and a determination is a direct measure of the amount of an alcohol present.

Reported methods (1) were for various reasons considered to be unsatisfactory. Some of them were required two to twenty-four hours for each determination. Some required a large volume of solvent. One (2) required only twenty minutes for the reaction with the acetyl chloride, without solvent, to be completed, but this one required dry ice, which was not readily available to the author.

The method finally employed made use of pure acetyl chloride and simple, readily-available equipment. The reaction was carried out in a 20-ml. bottle and the reagents were introduced through a tight-fitting stopper. Stoppers of various materials were tried. All, including neoprene, rubber and tygon, absorbed acetyl chloride to a certain extent. Rubber seemed to be the least objectionable in this respect, but satisfactory results depended upon the use of as small a stopper as possible and the control of the time of contact with the stopper. With suitable care check results of within $\pm 0.3\%$ were obtained.

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Experimental

Numerous preliminary experiments are, of course, omitted.

Equipment.—A 1-ml. tuberculin syringe, a 10-ml. syringe, two $\frac{5}{8}$ -inch, 25-gauge hypodermic needles, two 20-ml. bottles¹ with $\frac{1}{4}$ -inch openings at the neck and a supply of $\frac{1}{4}$ -inch rubber stopples².

¹The bottles used in this work had contained Eli Lilly and Company Physiological Salt Solution.

²Furnished by Commercial Solvents Corporation.

Procedure.—Two determinations were performed simultaneously. Each bottle was handled as follows: About 0.3 ml. of acetyl chloride was placed in the bottle and the stopple inserted. The bottle was shaken and let stand for five minutes³. The stopple was removed and the bottle half-filled with water. The bottle was shaken with the stopple in place; then the contents emptied. The bottle was filled with water, one-half poured out; then shaken with the stopple in place and emptied. It was then rinsed three times with small amounts of acetone and dried with a current of air. The stopples were placed in a small beaker and rinsed three times with acetone and air-dried for about five minutes. The stopple was inserted and fastened tightly. Using the tuberculin syringe, exactly 0.300 ml. of acetyl chloride was introduced through the stopple. In order to avoid parallax a piece of paper was glued onto the syringe opposite the 0.300 graduation. The bottle was shaken and let stand for five minutes. By means of the 10-ml. syringe, about 10 ml. of water was injected into the bottle and the bottle was shaken with the needle in place. About 11 ml. of air was withdrawn from the bottle into the syringe, which was then removed from the bottle. The stopple was removed and the contents of the bottle were poured into an Erlenmeyer flask. The bottle was filled with water, one-half emptied into the Erlenmeyer, the bottle shaken with the stopple in place and the remaining water poured into the Erlenmeyer. The contents of the Erlenmeyer were titrated with standardized alkali, using phenolphthalein indicator. This is the blank titration.

The bottles and stopples were rinsed and dried as described above and used for an actual determination, the only difference in procedure being that a weighed sample, sealed in a small, thin-walled glass bulb, was placed in the bottle before the stopple was inserted and that the glass bulb was broken by shaking after the addition of the acetyl chloride. If a series of determinations is interrupted for more than a few minutes, it is necessary to pretreat the rubber stopples again with acetyl chloride before continuing. Each day a new blank should be run.

Results.—Table I shows a series of consecutive determinations, except that the pure methanol was run along with a different series at a different time.

Summary

A procedure is described for the determination of methanol, using acetyl chloride as the reagent. The reagent which does not enter into ester-formation is hydrolyzed and titrated with standardized alkali. A 20-ml. bottle is used as the reaction vessel and the reagent is introduced quantitatively, by means of a syringe, through a rubber stopple in the bottle.

³If the stopples were not subject to about the normal exposure to acetyl chloride before starting, the first determination would give a low value.

TABLE I.

Material	Sample Weight	Titre N=.2618	Blank less Titre	Percent Methanol
	Blank	32.96		
	Blank	33.04		
	Av.	33.00		
4	.1345	31.80	1.20	8.0
4	.1525	31.69	1.31	7.6
7	.1391	29.72	3.28	21.0
7	.1779	28.82	4.18	20.9
8	.1266	27.50	5.50	38.6
8	.1259	27.58	5.42	38.2
9	.1103	25.74	7.26	58.6
9	.1327	24.47	8.53	57.1
	Blank	32.92		
	Blank	32.96		
	Av.	32.94		
Methanol	.0986	21.88	11.07	99.8

References

1. A list of references appears in an article by Petersen, J. W. Hedberg, K. W. and Christensen, B. E., Ind. Eng. Chem. Anal. Ed., **15**, 225 (1943), and in the following reference.
2. Christensen, B. E., Pennington, L. and Dimick, P. K., Ind. Eng. Chem. Anal. Ed., **13**, 821 (1941).