

Table II. Analysis of Synthetic Camphor

No.	Camphor Present %	Alcohol Present %	Refractive Index	Specific Gravity	Camphor Determined %	Camphor Variation %	Alcohol Determined %	Alcohol Variation %
1	10.00	85.56	1.3741	0.8275	9.92	-0.08	85.50	-0.06
1	10.00	85.56	1.3742	0.8279	9.98	-0.02	85.35	-0.21
1	10.00	85.56	1.3741	0.8277	9.90	-0.10	85.48	-0.08
2	10.15	77.00	1.3754	0.8549	10.15	0.00	77.00	0.00
2	10.00	85.56	1.3743	0.8278	10.08	+0.08	85.34	-0.22
2	10.40	84.00	1.3749	0.8321	10.33	-0.07	83.88	-0.12
3	9.70	79.00	1.3749	0.8501	9.75	+0.05	78.91	-0.09
3	10.00	85.56	1.3742	0.8278	9.98	-0.02	85.43	-0.13
3	10.00	86.00	1.3741	0.8250	10.03	+0.03	85.94	-0.06
4	9.30	84.00	1.3739	0.8341	9.31	+0.01	83.98	-0.02
4	10.00	85.54	1.3744	0.8277	10.17	+0.17	85.33	-0.21
4	11.10	81.00	1.3763	0.8405	11.22	+0.12	80.93	-0.07
5	8.00	80.00	1.3730	0.8486	8.00	0.00	80.15	+0.15
5	10.00	85.56	1.3742	0.8277	10.00	0.00	85.45	-0.11
5	10.90	80.00	1.3760	0.8447	10.85	-0.05	80.00	0.00
6	10.00	85.40	1.3743	0.8284	10.03	+0.03	85.18	-0.22
6	10.00	80.00	1.3751	0.8467	10.00	0.00	79.90	-0.10
6	10.50	85.60	1.3746	0.8250	10.54	+0.04	85.70	+0.10
7	10.00	85.40	1.3742	0.8286	9.91	-0.09	85.20	-0.20
7	10.00	86.00	1.3741	0.8250	10.07	+0.07	85.97	-0.03
7	9.70	79.00	1.3749	0.8501	9.75	+0.05	78.91	-0.09
8	10.00	85.40	1.3742	0.8286	9.91	-0.09	85.20	-0.20
8	10.50	85.60	1.3745	0.8250	10.45	-0.05	85.77	+0.17
8	9.70	79.00	1.3750	0.8500	9.82	+0.12	78.78	-0.22

lected from eight different sources; Table II shows the results of the analyses. Again these are in accord with the theoretical values.

SUMMARY

A chart has been constructed from which the percentages of alcohol and camphor in spirit of camphor may be determined when the refractive index and specific gravity of the spirit are known. Analyses of different samples of spirit of camphor, whether prepared from natural or synthetic camphor, by the proposed method show close agreement with the theoretical values.

LITERATURE CITED

- (1) Plein, E. M., and Poe, C. F., *IND. ENG. CHEM., ANAL. ED.*, **10**, 78-80 (1938).
- (2) Plein, E. M., and Poe, C. F., *J. Am. Pharm. Assoc.*, **32**, 89-95 (1943).
- (3) Schoorl, N., *Pharm. Weekblad.*, **66**, 977-86, 1001-9 (1929); *Pharm. Presse Wiss. prakt. Heft*, 1930, 33.
- (4) Weber, E., *Deut. Apoth. Ztg.*, **50**, 642-4 (1935).

Precision and Accuracy of Colorimetric Procedures as Analytical Control Methods

Determination of Aluminum

ALLEN L. OLSEN, EDWIN A. GEE, AND VERDA MCLENDON
Bureau of Mines, Eastern Experiment Station, College Park, Md.

A colorimetric procedure for the determination of aluminum, calculated and represented as aluminum trioxide and involving the formation of the red complex by the interaction of the aluminon reagent and the aluminum ion, has been developed to meet the special requirements in the rapid analysis of leach liquors in pilot-plant operations. The factors influencing color intensities have been investigated and the requisite techniques for a precision and an accuracy of a control character are described. Employing these techniques in the analysis of an aliquot of the leach liquor, precision and accuracy studies as applied to ordinary and refined laboratory techniques have been made on typical analytical data. Statistical reasoning based on the standard deviation is applied to the acquired data. Applying ordinary laboratory techniques, the average precision, measured by the average deviation of the single results from the mean, is of the order of 1% or 10 parts per 1000, while the overall accuracy is of the order of 1 to 3%.

NUMEROUS literature references (7, 8, 12) and recently published books (3, 6, 17) describe in detail the procedures involved in colorimetric determinations. Although the colorimetric method has been used for the rapid estimation of small quantities of many inorganic substances, not a great deal of emphasis has been placed on the precision and accuracy that might be expected in its use as an analytical control method. In quality control work, speed is so essential that precision and accuracy are often sacrificed; however, since intelligent conclusions in plant operations have to be based on the analytical data, it is essential to ascertain the precision and accuracy of the control methods.

Recent investigations in this laboratory have been concerned with the colorimetric procedures involving aluminum, titanium, silicon, and sodium. The procedures are, for the most part, adaptations of previously published methods; however, as a

matter of convenience, deviations from standard procedures are necessarily made from time to time, and the subsequent effects of the variables on precision and accuracy are briefly considered. Statistical reasoning based on the standard deviation is applied to the acquired data (1). The purpose of this investigation is therefore twofold: to describe satisfactory laboratory techniques in colorimetric procedures as applied to aluminum and to evaluate the precision and accuracy that might be expected in routine analyses.

The usual procedure in the colorimetric determination of aluminum involves the formation of the red complex by the interaction of the ammonium salt of aurin tricarboxylic acid (aluminon) and the aluminum ion in a carefully buffered solution (3). In the investigation of aluminum in plants, Winter, Thrun, and Bird (15) conclude that maximum color is obtained in the presence of 10% ammonium acetate when the solution is maintained at a temperature of 80° C. for 10 minutes and pH 4 (approximately). In the presence of 25 ml. of both ammonium acetate and ammonium chloride, they find that the dye changes color at about pH 7. Roller (10) states that the red color which aluminum ion gives with aurin tricarboxylic acid is much more sensitive if made at about pH 6.3 instead of in alkaline solutions as recommended by Yoe and Hill (16). The latter authors, investigating the procedure under different experimental conditions, cite five factors that affect the test for aluminum with aluminon: time, temperature, volume, concentration, and the presence of other ions. Lampitt, Sylvester, and Belham (5) suggest the use of glycerol to stabilize the lake formed. Thrun (13) has investigated the use of protective colloids in colorimetric determination of certain metals as lakes of dyes and recommends the use of a gum arabic solution to keep the aluminum lake of aurin tricarboxylic acid in solution.

The colorimetric method presented here for the determination of aluminum, calculated and represented as aluminum trioxide, has been developed at this station to meet the special requirements in the rapid analysis of leach liquors in pilot-plant operations. The sample taken for analysis must be free from inter-

Table I. Colorimeter Readings
(0.04 mg. of Al_2O_3)

Test Tube	No. 1	No. 2	Average
1	185	185	185
2	185	185	185
3	185	186	186
4	184	186	185
5 ^a	161	166	164
1a ^a	173	168	170
2a ^a	159	157	158
3a ^a	183	178	181
4a ^a	158	158	158
5a ^a	163	163	163
1b	187	186	187
2b	183	186	185
3b	184	187	186
4b	184	187	186
5b	185	187	186

^a Old test tubes; previous history unknown.

fering ions, which include ferric iron, beryllium, and chromium, since these form a lake similar to that formed by aluminum. Certain variations may be introduced to eliminate these interferences. Chromium lake, for instance, in acetate solution is rapidly decomposed by the addition of ammonia and ammonium carbonate (6). Several procedures may be followed for eliminating interfering iron (4, 9). Phosphate, if present in appreciable quantities, prevents the formation of aluminum lakes.

ANALYTICAL PROCEDURE

REAGENTS. Composite Solution. Dissolve 154 grams of ammonium acetate, 5 ml. of concentrated hydrochloric acid, 0.400 gram of ammonium salt of aurin tricarboxylic acid and 1 gram of gum arabic in water, and dilute to 1000 ml. Dissolve each reagent in a minimum quantity of distilled water, and add the ingredients of the composite in the order named. The aluminon reagent, weighed out to the nearest milligram, dissolves readily in cold water. To make accurate dilutions, the solution of gum arabic must be cautiously added; otherwise persisting foams will greatly alter the liquid level. The composite solution deteriorates with age, especially when exposed to the light; it therefore, must be protected from light when stored.

Standard Aluminum Solution. Dissolve 4.74 grams of aluminum chloride hexahydrate in 1000 ml. of water (1 ml. = 1 mg. of aluminum trioxide) and standardize gravimetrically (2).

Working Standard. Dilute 5 ml. of the standard to 500 ml. (1 ml. = 0.01 mg. of aluminum trioxide).

PROCEDURE. Discharge an aliquot of the previously diluted and acidified leach liquor (10 ml. of liquor and approximately 15 ml. of concentrated hydrochloric acid in 250 ml.), of an amount estimated to contain 0.01 to 0.06 mg. of aluminum trioxide, into a 25-ml. calibrated blood-sugar test tube by means of a pipet, add distilled water to the 12.5-ml. mark, and thoroughly mix the contents. Add 10 ml. of the composite solution by means of an automatic pipet and sufficient water to bring the meniscus to the 25-ml. mark. Mix the contents of the tube well and place in a boiling water bath for precisely 10 minutes. Cool the tube and contents in running tap water for 5 minutes, mix again, and determine the color absorption with the Klett-Summerson photoelectric colorimeter. A filter of range 500 to 570 millimicrons is employed, since a spectrophotometric study of the color in question shows a maximum absorption at 530 $m\mu$ in the red complex.

Since absorption of the red color is not a linear function of the aluminum trioxide concentration, a calibration curve must be established. Quantities of the working standard, equivalent to 0.01, 0.02, 0.03, 0.04, 0.05, and 0.06 mg. of aluminum trioxide, are discharged into blood-sugar test tubes, and the lakes are formed in the usual manner.

Procedures for the gravimetric analysis of aluminum involve the use of a modification of the quinolate method (2).

From the standpoint of accuracy, ease of manipulation, and rapidity of technique, preliminary investigations indicated that the method of dilution was entirely satisfactory. Calibration of twenty blood-sugar test tubes resulted in an average precision of 0.2% or 2 parts per 1000. No detectable difference in colorimeter reading could be observed in comparing procedures involving pipets, burets, and 25-ml. blood-sugar test tubes.

In an investigation on the factors influencing color intensities, certain anomalous results were obtained in establishing the standardization curve (Table I). Even though these tubes were

thoroughly cleaned with chromic acid cleaning solution, it is apparent that only new tubes gave reproducible results. The previous history of the remainder of tubes was unknown. Table II shows the effects of chemically clean test tubes on the reproducibility factor. Tubes in Series I of this table were cleaned with chromic acid cleaning solution; tubes of Series II were cleaned by treating successively with chromic acid, water, ethyl alcohol, benzene, and water; and tubes of Series III were treated with hot chromic acid, water, and alkaline cleaning mixture (14) and rinsed thoroughly with distilled water. Thus, to obtain reproducibly accurate results the test tubes must be chemically clean. In all subsequent colorimetric measurements, new tubes only are used, and these are cleaned, using the procedure as established for Series III.

The length of time in the boiling water bath has a marked effect on the color intensity, as shown in Figure 1. The technique of heating at water-boiling temperatures is employed to increase greatly the rate of color development, and since the color intensity varies with the time, the tubes in all of these investigations were heated precisely 10 minutes.

Table II. Cleaning Effects on Blood-Sugar Test Tubes

Test Tube ^a	Colorimeter Readings (0.04 mg. of Al_2O_3)		
	Series I	Series II	Series III
11	203	196	190
12	192	188	188
13	169	173	185
14	172	178	187
15	175	180	185
11a	163	170	183
12a	187	186	182
13a	188	188	183
14a	167	169	183
15a	169	170	183

^a Old test tubes; previous history unknown.

The effect of varying quantities of composite on the color intensity is shown in Figure 2. Since the quantity of composite added influences the color intensity, exactly 10 ml. of the aluminon reagent were added from an automatic pipet.

Since the temperature of the sample and reagents is a factor in this method, a control of $\pm 5^\circ \text{C}$. of the solution temperature at the time of standardization should be maintained. Several degrees above and below that at which the curve is established result in no serious error. High temperatures promote color development, with attendant high aluminas, while lower temperatures have the opposite effect.

In the preparation of the composite solution, quantitative and qualitative techniques were applied to several sources of the re-

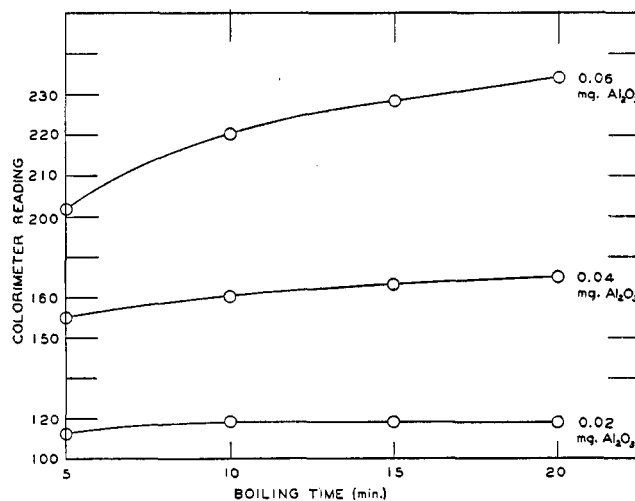


Figure 1. Effect of Heating Time on Color Intensity

agent. To reproduce the values of previously established standardization curves fairly accurately, it became necessary to weigh out the material on a quantitative basis. An Eastman product appeared to give fairly consistent values. Taylor-Austin (12), recognizing the variations in the color produced by the method, suggests a restandardization whenever a fresh supply of the solid reagent is put into use. Scherrer and Smith (11) state that a satisfactory reagent may be synthesized. However, in view of these variabilities and the fact that the composite undergoes a marked change on standing, even when protected from light, the prime necessity of carrying along a standard in routine analysis cannot be overemphasized. It is common practice in this laboratory to establish a new curve when it is observed that the reading of the standard, when compared with the curve, is in error by an amount greater than 4 or 5%. In the desired concentration range, 0.04 mg. of alumina per 25 ml., this represents 6 or 7 scale divisions. For close control work, especially if the curve has not been determined recently, moderate success has been realized by evaluating the scale divisions in the desired concentration range in terms of milligrams of alumina; thus, by running a standard in the concentration range of the unknown, one can calculate the alumina from the colorimeter reading. Obviously, since the milligrams per unit vary over different parts of the curve as well as for different curves, no permanent values should be assessed to each unit.

PRECISION AND ACCURACY

The precision and accuracy of the colorimetric method are conveniently studied by applying the techniques considered in the foregoing paragraphs to the analysis of a leach solution. An initial investigation was concerned with a factor of reproducibility of results. For this purpose two leach liquors, previously acidified and diluted (10 ml. in 250 ml.) were divided into five portions each, and a 1-ml. aliquot (2 ml. in 250 ml.) of each sample was taken for the measurement. The alumina content, recalculated by applying an appropriate factor for dilution (125), was measured over a period of several weeks. Table III, representing ordinary and refined laboratory techniques, shows what might be expected in the way of precision for 10 typically representative

Table III. Analysis of Leach Liquor

Test No.	Mg./ml.	d	(d ² × 10 ⁶)
Precision of Method under Ordinary Conditions			
1	5.11	-0.063	3969
2	5.23	+0.057	3249
3	5.19	+0.017	289
4	5.23	+0.057	3249
5	5.11	-0.063	3969
6	5.25	+0.077	5929
7	5.14	-0.033	1089
8	5.14	-0.033	1089
9	5.14	-0.033	1089
10	5.19	+0.017	289
Av. = \bar{X}	5.173		$\Sigma d^2 = 24210 \times 10^{-6}$
			$\sqrt{\frac{\Sigma d^2}{10}} = \pm 0.049 = \sigma_0$
$\bar{X} \pm \sigma = 5.173 \pm 0.053$ ($P_s = 0.99$, 10 observations)			
Av. of gravimetric data = 5.114 mg. (Al ₂ O ₃) per ml.			
Precision of Method under Best Conditions			
1	5.11	+0.018	324
2	5.08	-0.012	144
3	5.11	+0.018	324
4	5.04	-0.052	2704
5	5.08	-0.012	144
6	5.08	-0.012	144
7	5.14	+0.048	2304
8	5.07	-0.022	484
9	5.09	-0.002	4
10	5.12	+0.028	784
Av. = \bar{X}	5.092		$\Sigma d^2 = 7369 \times 10^{-6}$
			$\sqrt{\frac{\Sigma d^2}{10}} = \pm 0.027 = \sigma_0$
$\bar{X} \pm \sigma = 5.092 \pm 0.029$ ($P_s = 0.99$, 10 observations)			
Av. of gravimetric data = 5.124 mg. (Al ₂ O ₃) per ml.			

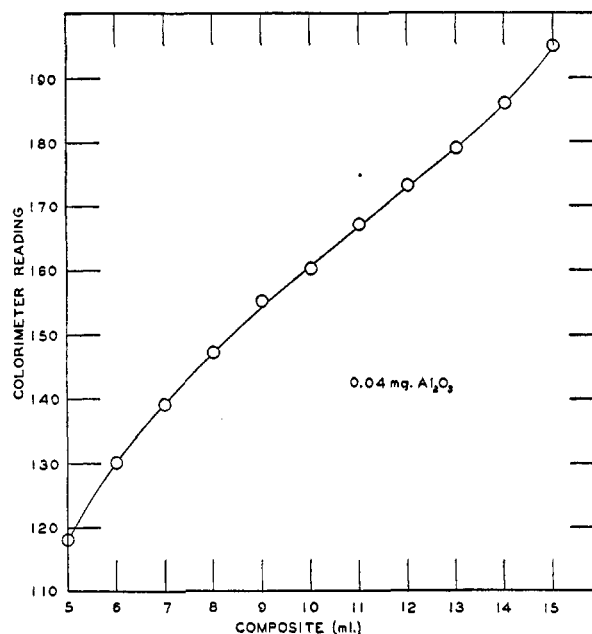


Figure 2. Effect of Varying Quantities of Composite on Color Intensity

values. The method of evaluating the factor of precision is that derived from consideration of results set up by A.S.T.M. (1). As shown in the table, the numerical results are based on the fact that 99 in 100 limits are used and that these results are based completely on the evidence contained in 10 determinations. The accuracy of the method is determined by making a comparison with gravimetric results; gravimetric data for 10 different leach liquors are given in Table IV.

Table IV. Analysis of Leach Liquors

Accuracy of method under ordinary conditions

Test No.	Gravimetric Mg./ml.	Colorimetric Mg./ml.	pH	Error %
1	4.113	4.23	6.0	<3
2	3.468	3.43	6.0	1
3	3.640	3.70	6.0	2
4	3.589	3.63	6.0	>1
5	3.637	3.65	6.0	<1
6	3.926	3.93	...	0
7	3.831	3.97	6.0	3
8	3.855	3.82	6.0	1
9	3.732	3.62	6.0	3
10	3.977	3.97	...	0

DISCUSSION

The expression, $P_s = 0.99$ (statistical probability), cited in Table III implies that a value for a was chosen such that, in 99 chances out of 100, one might expect the ranges bounded by the computed limits to include, of the universe sampled, the objective average, \bar{X}' .

From the data in Table III, it is apparent that the colorimetric method should give an average precision, measured by the average deviation of the single results from the mean, of approximately 1%, or 10 parts per 1000. On the basis of the gravimetric value, this represents an accuracy of 1.1%, or 11 parts per 1000. The precision and accuracy are increased by employing refined techniques. In this case special attention was given to temperature control, accurate aliquoting and pipetting, and precise establishment of the standardization curve. However, to attain this precision and accuracy, speed was materially sacrificed. In this case, the average precision becomes 0.6% or 6 parts per 1000. When compared with the gravimetric value, this represents an accuracy of 0.6% or 6 parts per 1000.

The accuracy of the colorimetric method is best judged from the data in Table IV. It is apparent that the accuracy of the method is of the order of 1 to 3%; however, in routine work an occasional 4% error has been observed. In view of the fact that the accuracy is inextricably tied in with the standardization curve, the importance of precise establishment of the calibration curve cannot be overemphasized. If the curve were recently established, then the accuracy and precision become nearly identical if put on the basis of a single analysis. This necessarily follows, since the method involves an empirical comparison against a calibration curve. It is obvious that a higher degree of accuracy will be obtained if, in the preparation of the solution for the colorimetric determination, the concentration of the unknown is approximately adjusted so as to fall in the range above 0.04 mg. per 25 ml.

A further consideration of Table IV reveals the fact that the leach liquors, having been previously acidified with approximately 15 ml. of concentrated hydrochloric acid, when aliquoted to the correct concentration in the presence of excess ammonium acetate, yield a reproducible pH (6.0).

Undoubtedly, colorimetric procedures may be applied for the determination of any element in any given amount by taking suitable aliquot portions for the measurement of the final color; however, applying such a procedure the degree of accuracy will fall markedly as the amount of sample, represented by the aliquots, becomes smaller and smaller. Application of the colorimetric process as a method of analytical control must be decided in terms of the effective range of accuracy by the individual analyst after carefully considering the problem at hand.

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LITERATURE CITED

- (1) Am. Soc. Testing Materials, "Manual on Presentation of Data", 3rd printing, p. 41, Philadelphia, 1940.
- (2) Hillebrand, W. F., and Lundell, G. E. F., "Applied Inorganic Analysis", p. 116, New York, John Wiley & Sons, 1929.
- (3) Johnson, W. C., et al., Technical Staff, "Organic Reagents for Metals", London, Hopkin and Williams, 1938.
- (4) Kul'berg, L. M., and Rovinskaya, E. I., *Zavodskaya Lab.*, 9, 145 (1940).
- (5) Lampitt, L. H., Sylvester, N. D., and Belham, P., *Analyst*, 57, 418 (1932).
- (6) Mellan, I., "Organic Reagents in Inorganic Analysis", Philadelphia, Blakiston Co., 1941.
- (7) Mellon, M. G., *IND. ENG. CHEM., ANAL. ED.*, 11, 80 (1939).
- (8) Müller, R. H., *Ibid.*, 11, 1 (1939).
- (9) Musakin, A. P., *Zavodskaya Lab.*, 9, 507 (1940).
- (10) Roller, P. S., *J. Am. Chem. Soc.*, 55, 2437 (1933).
- (11) Scherrer, J. A., and Smith, W. H., *J. Research Natl. Bur. Standards*, 21, 113 (1938).
- (12) Taylor-Austin, E., *J. Soc. Chem. Ind.*, 60, 29 (1941).
- (13) Thrun, W. E., *IND. ENG. CHEM., ANAL. ED.*, 2, 8 (1930).
- (14) Willard, H. H., and Furman, N. H., "Elementary Quantitative Analysis", 3rd ed., p. 15, New York, D. Van Nostrand Co., 1940.
- (15) Winter, O. B., Thrun, W. E., and Bird, O. D., *IND. ENG. CHEM., ANAL. ED.*, 51, 2721 (1929).
- (16) Yoe, J. H., and Hill, W. L., *J. Am. Chem. Soc.*, 49, 2395 (1927).
- (17) Yoe, J. H., and Sarver, L. A., "Organic Analytical Reagents", New York, John Wiley & Sons, 1941.

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Flow Characteristics of Dispersions of Cotton and Regenerated Cellulose Rayon Fabrics in Cuprammonium Their Significance in Fluidity Calculations

VIOLA C. JELINEK¹, Bureau of Human Nutrition and Home Economics, U. S. Department of Agriculture, Washington, D. C.

Flow-pressure and fluidity-velocity gradient graphs were used to determine the flow properties of cuprammonium dispersions of cellulose fabrics and to evaluate the method of calculating the fluidity values. The limits of application of the kinetic energy and velocity gradient adjustments were determined for cellulose-cuprammonium dispersions, under experimental conditions very similar to those recommended by the American Society for Testing Materials. The viscometer and buret consistometer were compared in the fluidity technique.

THE fluidity determination of cellulose dispersed in cuprammonium reagent is an important technique used in the study of cotton and regenerated cellulose rayon fabrics. It is a sensitive method for measuring the extent of degradation of cellulose. A linear relationship between fluidity values and service (11, 12) has been demonstrated in serviceability studies of cotton and rayon fabrics which have been subjected to wear and laundering. Raw cotton fibers dispersed in the cuprammonium solvent exhibit a lower fluidity than deteriorated cellulose.

The purpose of this study was to investigate the flow characteristics of cuprammonium dispersions of cotton and regenerated cellulose rayon fabrics over a wide range of fluidity values. The flow properties of cellulose-cuprammonium dispersions heretofore have been studied only in limited scope. It is important to

know which cellulose-cuprammonium dispersions are true viscous liquids and which exhibit anomalous flow properties. This information is fundamental in calculating the fluidities of these liquids.

The flow characteristics of the cellulose-cuprammonium dispersions were determined by means of flow-pressure and fluidity-velocity gradient graphs. As a result of the study of the flow properties of these dispersions, the limits of application of the kinetic energy and velocity gradient adjustments were determined. A comparison was made of the fluidity values obtained with the viscometer and the buret consistometer, and the appropriate instrument for the cellulose-cuprammonium fluidity determination was found to be dependent on the flow characteristics of the dispersion.

VISCOMETERS AND METHODS OF CALCULATION OF FLUIDITY VALUE

Two types of capillary tube viscometers are ordinarily used in the fluidity determination of cellulose-cuprammonium dispersions. Figure 1, A, shows the type of viscometer which delivers one or two volumes of liquid, and is recommended by the National Bureau of Standards (10), the American Society for Testing Materials (1), and the British Fabrics Research Committee (7). B is essentially the buret consistometer of Herschel and Bulkley (8) with attachments described by Conrad (6) and permits the discharge of a number of quantities in one determination. The buret consistometer is used in the Bureau of Human Nutrition and Home Economics (13) and Agricultural and Industrial Chemistry (6), U. S. Department of Agriculture.

¹ Present address, Research Laboratories, Merck & Co., Inc., Rahway, N. J.