Journal of Research of the National Bureau of Standards Vol. 45, No. 2, August 1950 Research Paper 2116

Cotton Powder for Infrared Transmission Measurements[1]

By Florence H. Forziati, Walter K. Stone, John W. Rowen, and William D. Appel

Cotton cut in a Wiley mill to pass a 20-mesh screen was ground in a vibratory ball mill similar to one that has been used in Germany and Holland. Contamination of the cotton was practically eliminated by using a chromium-plated hardened steel jar and chromium alloy balls. The jar holder is held by a slip ring instead of being bolted in place. The jar and holder automatically rotate slowly on their axis, and this motion counteracts the tendency of the cotton in the jar to settle and grind nonuniformly. The jar is cooled by blowing air over it and becomes barely warm to the touch.

Five grams of dried cotton disintegrated rapidly during the first 15 minutes of milling. The largest particles remaining after 30 minutes of milling were about 10 microns in major dimension, and there was little reduction of the maximum size with longer milling. Cuprammonium fluidity of the cotton increased rapidly in the first hour of milling and more gradually thereafter. The carboxyl content of the cotton increased very slowly with time of milling and reached only about 0.2 percent after 8 hours. The moisture regain of the cotton at 65-percent relative humidity at 21° C increased rapidly during the first hour of milling, from 7.1 to 12.5 percent, and then remained practically constant. X-ray diffraction measurements showed that the cellulose was converted almost completely to the amorphous form in 30 minutes, and that it underwent little change thereafter.

The powdered cotton obtained from the vibratory ball mill was mulled in mineral oil. The resulting paste was injected into rock salt cells for infrared absorption measurements. The powder worked reasonably well in this procedure, distinctly better than the coarse powders obtained by other methods of grinding. No significant differences were found in the infrared absorption of a regenerated cellulose film, the cotton ground in a Wiley mill to 200 mesh, and cotton ground in the vibratory ball mill for periods of time from 15 minutes to 8 hours.

It is concluded that the vibratory ball mill, as modified, reduces cotton, rapidly and completely, to a very fine powder, suitable for infrared transmission measurements and other purposes. Milling results in practically negligible oxidation of the cellulose, but in a marked decrease in degree of polymerization, and in almost complete conversion of crystalline to amorphous cellulose.

I. The Problem

The first problem arising in the attempt to apply infrared spectrophotometry to cotton cellulose was to prepare the cotton in a form suitable for introduction into the beam of the spectrophotometer. Microspectrophotometers applicable to single cotton fibers were not available at the time the work was started, though promising instruments are now being developed [1, 2, 3, 4].[2] Spectra obtained from fibers laid side by side were not encouraging. Preparation of films from the cotton, for example by converting it to cellulose acetate and then, as in previous work [5], casting a film and deacetylating it, did not seem to answer the problem, not only because of the changes in structure that would result but because such a procedure would not be applicable to some degraded cottons. It was, therefore, decided to try to reduce the fibers to a powder and measure the absorption of the powder in a mat or in suspension in a suitable liquid.

Several well-known methods for grinding materials were tried. They included grinding in a Wiley mill in which the material is cut between fixed and rapidly moving blades, in a ball mill using both stone and steel balls in a porcelain jar, and in a Waring Blendor. An ultrasonic generator, operating at 8 kc and 250 ma, was tried. The products obtained by these methods contained much coarse material. A method that would reduce the entire sample to a finely divided state, without contamination and with a minimum of chemical change, was desired.

The work of Hermans and Weidinger [6] on cellulose, ground in a vibratory ball mill, suggested the possibility of this type of machine for this purpose. This mill appeared to be quite different in its grinding action from an ordinary ball mill [7]. Examination of a sample of rayon ground in this type of mill led to the construction of a similar mill. Several changes in construction were made in order to fit the mill for this work.

This report describes the mill and discusses the changes that cotton underwent when ground in it.

II. Vibratory Ball Mill

Descriptions of the vibratory ball mill, the principle of its action, and a mathematical analysis of the motions of the balls in it, have been published by Kiesskalt [7] and Bachmann [8]. Therefore, only a brief description of the mill built at the National Bureau of Standards is given here.[3]

The mill is illustrated in figures 1, 2, and 3. It consists of a horizontal shaft connected at one end, by means of a flexible coupling, to a ¼-horsepower motor having a speed of 1,800 rpm, and at the other to an eccentric weight. The weight rotates in a

[1] A report of work done under cooperative agreement with the United States Department of Agriculture and authorized by the Research and Marketing Act. The agreement is being supervised by the Southern Regional Research Laboratory of the Bureau of Agricultural and Industrial Chemistry.

[2] Figures in brackets indicate the literature references at the end of this paper.

[3] Working drawings of the mill built at the National Bureau of Standards may be obtained upon request to the National Bureau of Standards, Textiles Section, Washington 25, D. C.

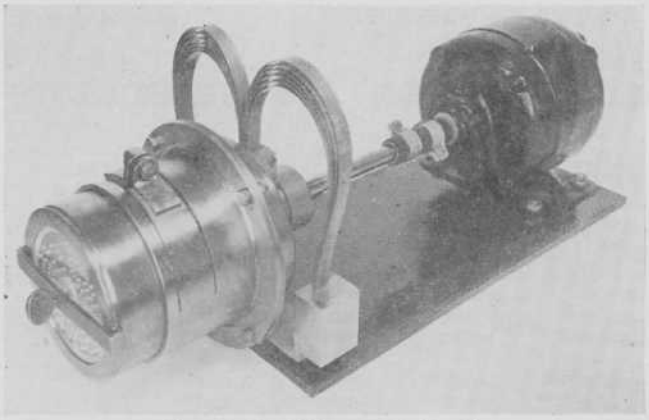

FIGURE 1. *Vibratory ball mill.*

Jar shown with transparent plastic cover instead of chromium-plated steel cover; safety guard removed from shaft.

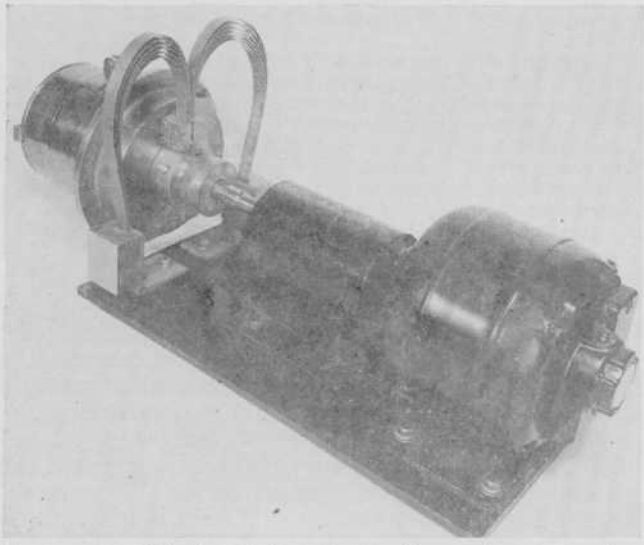

FIGURE 2. *Vibratory ball mill, showing spring suspension; safety guard for shaft in position.*

housing suspended from leaf springs. A cylindrical jar of approximately 1-liter capacity slips into a holder attached to the housing. The housing, with attached holder and jar, is moved in a circular path by the rotation of the eccentric weight. Steel balls in the jar are set into rapid motion by this movement, and their collisions grind the material placed in the jar with them.

The cellulose milled in P. H. Hermans' mill contained inorganic material from the ceramic jar. Hermans suggested the use of steel balls to reduce contamination. Not only was this done, but the jar was machined from a solid block of Stentor tool steel. Trial runs were carried out with this jar, three-fourths full of ¼-in. steel balls, on 5-g samples of cotton, previously ground in a Wiley mill to pass a 20-mesh screen. At the close of a 3-hr run, the balls had lost their polish, while the sample was gray in color and contained about 0.4 percent by weight of iron.

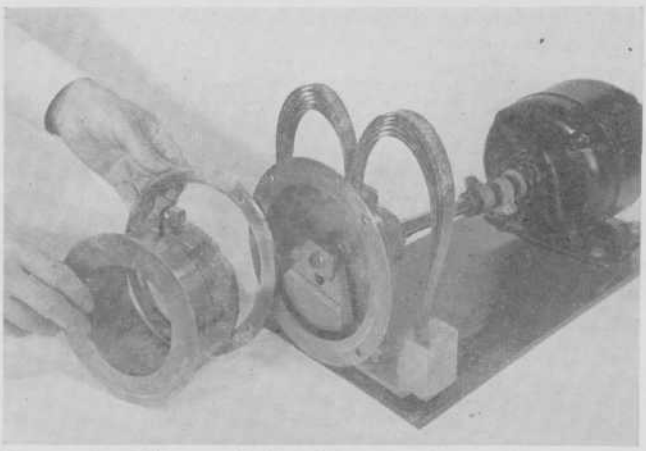

FIGURE 3. *Vibratory ball mill, partly disassembled to show, from left to right, the jar holder, slip ring, and eccentric weight on the end of the shaft in the weight housing.*

The jar was then hardened to "C" 61 Rockwell and chromium plated. The steel balls were replaced with chrome alloy balls of hardness of approximately "C" 64. With this combination, the contamination of 5g of cotton was less than 0.05 percent in a run of 8 hr.

Experience with the mill showed that the material being ground tended to settle to the lower side of the jar. In order to insure uniform pulverization, it was necessary to stop the machine at frequent intervals and redistribute the contents of the jar by rotating it 180 degrees. Observations, through a plastic cover, showed that the balls moved slowly in a direction opposite to that of the eccentric weight. This suggested that the jar might rotate in the same direction as the balls if it were free to do so and thus automatically redistribute the charge. Accordingly, a slip ring, shown in figures 1 and 3, was substituted for the bolts with which the jar holder was originally attached to the weight housing. With this change, the jar rotates at a rate of approximately 1 rpm, and the material being ground does not settle out.

III. Changes in Cotton During Grinding

Empire cotton (lot AP845), supplied by the Southern Regional Research Laboratory, U. S. Department of Agriculture, was used in studying the effects of milling in the modified vibratory ball mill. This cotton was extracted for 8 hr in a Soxhlet with ethanol, washed with distilled water, dried in air at room temperature, and ground in a Wiley mill to pass a 20-mesh screen. Five-gram specimens were then dried for 1 week over magnesium perchlorate and placed in the jar of the vibratory mill with enough ¼-in. chrome-steel balls to fill it three-fourths full. In order to minimize heating of the cotton during grinding, a fan was used to blow the room air over a jar. Without this cooling, the temperature of the jar and balls rose to 65° C and higher in 3 hr of continuous milling. With the cooling, the jar was barely warm to the touch at the end of 8 hr. Cotton milled for periods of time

ranging from 15 min to 8 hr, was examined with respect to particle size, fluidity in cuprammonium solution, carboxyl content, and moisture regain after exposure to air at 65-percent relative humidity at 21° C. In addition, X-ray diffraction and infrared transmission measurements were made. The results follow.

1. Particle Size

Microscopic examination of the products mulled in a water-white mineral oil, figure 4, showed that the fibers disintegrated rapidly during the first 15 min of milling. Some relatively large fragments were present after 15 min, but not after 30 min, of milling. The largest particles remaining after 30 min were about 10 μ in major dimension. There was little or no reduction of the maximum size of the particles with longer milling. Although mulling produced a limited amount of fiber disintegration, it was used in the microscopic work to overcome the tendency of the particles of the milled samples to form aggregates.

2. Cuprammonium Fluidity

The fluidity of the products in cuprammonium solution, measured by the Wilson and Launer modification of the standard method [9], is shown in table 1 and figure 5. An extremely rapid decrease in the length of the cellulose chains is indicated by the increase in fluidity. This is in agreement with the results reported by Hess and his coworkers [10, 11, 12]. They showed that the kinetic energy of the balls is converted directly into molecular vibrational energy of the material under impact. In addition, they found the degradation, as measured by solution viscosity, to be independent of the temperature of milling between 0° and 90° C.

TABLE 1. *Effects of the milling on cotton*

Milling period	Cuprammonium fluidity	Carboxyl	Moisture regain [a]
Hours	*Rhes*	*Percent* [b]	*Percent*
0	5.4	0.00	7.1
¼	15.2	.03	10.3
½	25.3	.03	11.9
¾	30.4	.03	12.0
1	36.9	.03	12.7
2	46.1	.08	12.6
4	51.9	.11	12.8
8	57.7	.22	12.5

[a] At 65% relative humidity and 21° C.
[b] Calculated on oven-dray basis.

3. Carboxyl Content

The carboxyl contents of the products, determined by the method of Yackel and Kenyon [13], are shown in table 1 and figure 5. The increase in carboxyl content in the first hour of milling was extremely small. The small increase in 8 hr of milling supports the view of Hess and his coworkers [10, 11] that the effect of this type of milling on the cellulose is primarily mechanical.

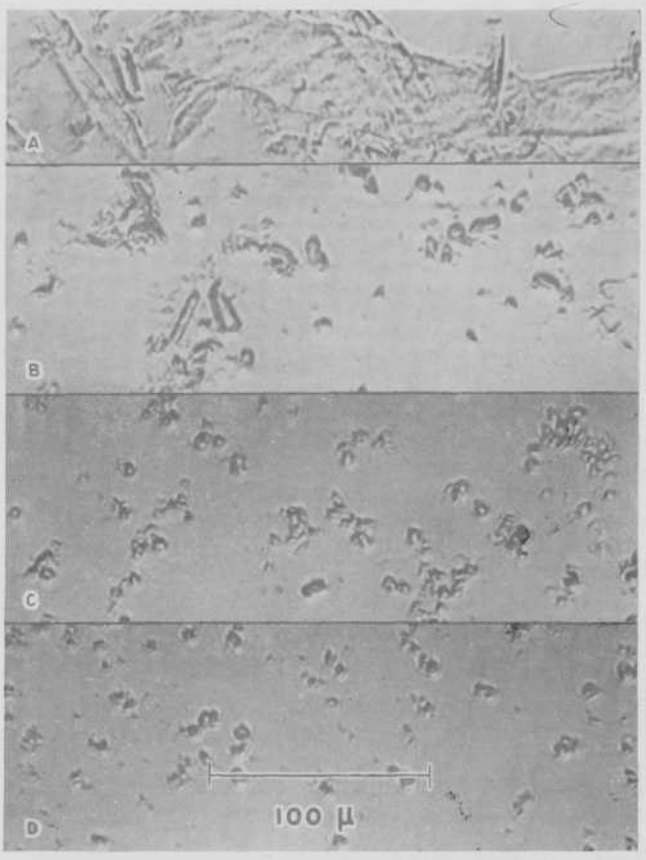

FIGURE 4. *Cotton that has been ground and then mulled in mineral oil.*

A, Ground in Wiley mill to pass 20-mesh screen; *B*, as in *A* and, in addition, ground in vibratory ball mill for 15 minutes; *C*, as in *B* but ground in vibratory ball mill for 30 minutes; *D*, as in *B* but ground in vibratory ball mill for 1 hour.

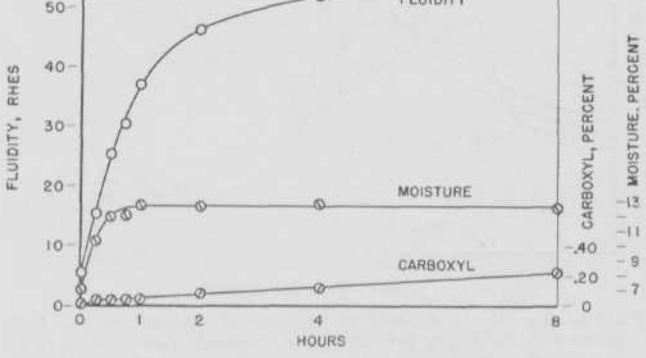

FIGURE 5. *Cuprammonium fluidity, moisture regain at 65-percent relative humidity at 21° C, and carboxyl content of cotton verses time of milling in the vibratory ball mill.*

4. Moisture Regain

The moisture regain of the powders when exposed to air of 65-percent relative humidity at 21° C after grinding, table 1 and figure 5, increased rapidly during the first hour of milling, from 7.1 to 12.5

percent, and remained practically constant with increase in time of milling up to 8 hr. The moisture capacity of cellulose is generally considered to be proportional to the amorphous fraction of the cellulose. If this is so, the milling increased the proportion of amorphous cellulose in the sample. The fact that no substantial increase in moisture regain occurred after the first hour of milling indicates that the crystalline material was converted to noncrystalline during the first hour.

5. X-Ray Diffraction

X-ray diffraction patterns of the powders, figure 6, were obtained with a Geiger counter spectrometer, operating at 40 kv and 15 ma and using copper radiation, $\lambda = 1.54050$ A. The powders were packed in a flat specimen holder 0.8 mm deep and 13.5 mm in diameter.

A rapid and profound change in the X-ray diffraction pattern of the cotton resulted from milling in the vibratory ball mill. The 20-mesh control sample gave the X-ray diffraction pattern characteristic of the crystal lattice of cellulose I (native cellulose). The patterns obtained with samples that were milled for periods of time ranging from 30 min to 8 hr showed only the broad diffuse band characteristic of amorphous cellulose [14]. The position of the bands in the pattern of the sample that had been milled for 15 min indicates that cellulose II (mercerized cellulose) is formed during the early stages of milling in the vibratory ball mill and is then converted to amorphous cellulose.

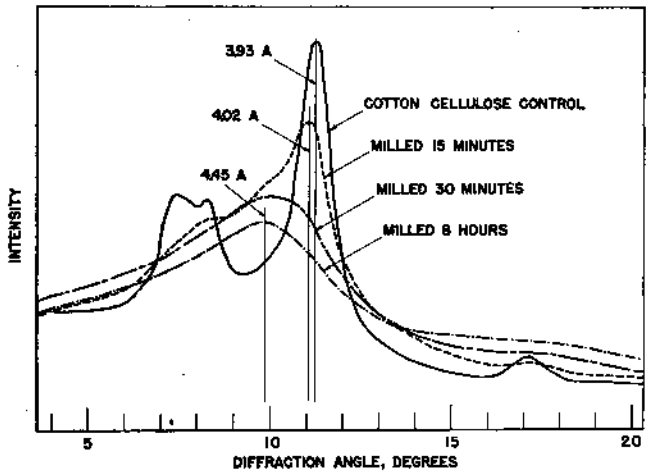

FIGURE 6.—*X-ray diffraction patterns of cotton that has been ground in the Wiley mill to pass a 20-mesh screen and then in the vibratory ball mill for 15 minutes, 30 minutes, and 8 hours.*

The figures shown on the curves give the interplanar spacings corresponding to the most intense bands.

6. Infrared Absorption

The powders were prepared for infrared absorption studies by mulling in water-white mineral oil and injecting into demountable rock salt cells.

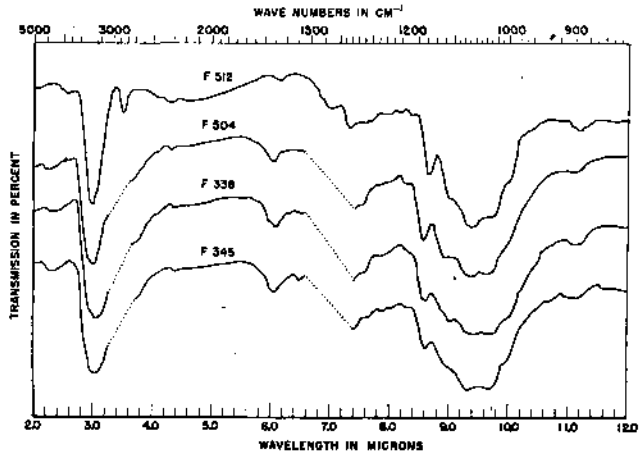

FIGURE 7. *Infrared absorption spectra.*

Dotted lines are shown in the regions obscured by the absorption of the mineral oil. F512, Regenerated cellulose film; F504, cotton ground in Wiley mill to pass 200-mesh screen and then mulled in mineral oil; F338, cotton ground in vibratory ball mill for 15 minutes and then mulled in mineral oil; F345, same as F338 except that cotton was ground in the vibratory ball mill for 8 hours.

Cells of two or more thicknesses were used for each powder. Spectra, figure 7, were obtained with a Baird spectrophotometer. The results show no significant differences between cotton that had been ground in a Wiley mill to pass a 200-mesh [4] screen, cotton that had been ground in the vibratory ball mill for periods of time ranging from 15 min to 8 hr, and a film of regenerated cellulose [5]. Thus, such functional groups as may be introduced by milling the cotton in the vibratory ball mill are not detectable in the infrared absorption spectrum. The absence of an absorption band at 5.75 μ, the region of the spectrum in which the C=O of the carboxyl groups absorbs, is in agreement with the very low values for carboxyl content, obtained by chemical means. Such decreases in degree of polymerization as are indicated by the cuprammonium fluidities would not be expected to result in changes in infrared absorption. Thus, the infrared absorption measurements constitute additional evidence for the conclusion of Hess and his coworkers [10] that the degradation produced by the mill is hydrolytic rather than oxidative. The possibility is not eliminated, however, that oxidation may have resulted in the formation of groups that were not detected by the infrared absorption measurements.

IV. Conclusions

The results indicate that the vibratory ball mill, as modified, reduces the cotton rapidly and completely to a very fine powder suitable for infrared transmission measurements and other purposes. Milling results in practically negligible oxidation of the cellulose, but in a marked decrease in degree of polymerization and in conversion of crystalline to amorphous cellulose.

[4] Due to excessive scattering of light, absorption measurements could not be made on the 20-mesh control.

The authors express their appreciation of the help received from P. H. Hermans, Utrecht, The Netherlands. He ground material for us in his mill and supplied drawings of the mill. The authors are indebted to the machine shop of the Bureau for assistance in the design and construction of the mill at the Bureau, to Sanford Newman and Emil Borysko for the preparation of photomicrographs, and to Howard E. Swanson for the X-ray diffraction patterns.

V. References

[1] C. R. Burch, Proc. Phys. Soc. **59,** 1, 47 (1947).
[2] R. Barer, A. R. H. Cole, and H. W. Thompson, Nature **163,** 198 (1949).
[3] E. R. Blout, G. R. Bird, and D. S. Grey, J. Opt. Soc. Am. **40,** 304 (1950).
[4] L. V. Foster, Anal. Chem. **21,** 432 (1949).
[5] J. W. Rowen, C. M. Hunt, and E. K. Plyler, J. Research NBS **39,** 133 (1947) RP1816.
[6] P. H. Hermans and A. Weidinger, J. Am. Chem. Soc. **68,** 2547 (1946).
[7] S. Kiesskalt, Z. Ver. Deut. Ing. Beih. Verfahrenstechnik **1936,** No. 1, 1 and DRP 619,662; 620,721.
[8] D. Bachmann, Z. Ver. Deut. Ing. Beih. Verfahrenstechnik **1940,** No. 2, 43.
[9] H. F. Launer and W. K. Wilson, Anal. Chem. **22,** 455 (1950).
[10] K. Hess, H. Kiessig, and J. Gundermann, Z. Physik. Chem. **B49,** 64 (1941).
[11] K. Hess, E. Steurer, and H. Fromm, Kolloid Z. **98,** 148, 290 (1942).
[12] K. Hess, Z. Ver. Deut. Ing. Beih. Verfahrenstechnik **1943,** 61; Chem. Zentr. **1944,** I, 6 and Chem. Abs. **39,** 2905[9] (1945).
[13] E. C. Yackel and W. O. Kenyon, J. Am. Chem. Soc. **64,** 121 (1942).
[14] P. H. Hermans and A. Weidinger, Bul. Soc. Chim. Belg. **57,** 123 (1948).

WASHINGTON, April 30, 1950.

Journal of Research of the National Bureau of Standards Volume 45, No. 2, August 1950 Research Paper 2117

Gravimetric Analysis of Exhaust Gas From Gas Turbine Combustion Chambers[1]

By Fillmer W. Ruegg and Carl Halpern

Because of the high air-fuel ratio used in combustion chambers of gas turbines, the concentration of products of combustion is so low that standard volumetric methods of analysis have proved unreliable. A gravimetric method of anaylsis was developed and applied to the problem, not to identify all of the constituents, but primarily to determine the efficiency of the combustion process. In this method the products of complete combustion, water and carbon dioxide, are separated from each other and from the remainder of the sample, which is then passed into a furnace to burn the combustible components. Carbon dioxide and water are determined by change of weight of solid absorbents. Experiments showed that the method may be used to provide accurate information about the magnitude of the loss of heat due to incomplete combustion, and partial information about the nature of the components of the exhaust gas.

I. Introduction

The primary objective of application of the combustion process in combustion chambers of gas turbines, and in fact in nearly all of its applications, is the release of energy in the fuel to heat the working fluid from its initial to its final temperature. Change of temperature of the working fluid is an indication of its enthalpy change, but temperature alone is inadequate to relate this enthalpy change to the energy available in the fuel. In order to obtain such a relation, calculation of a heat balance involving rates of flow as well as temperature must be made. It is inconvenient or perhaps impossible in some cases to make accurate measurements of these quantities, and it is in such instances that gas analysis may be called upon to supply the desired information about the efficiency of the combustion process. Even in cases where the heat balance can be calculated from experimental data, the measurements are subject to uncertainties, and an accurate method of analysis of the exhaust gas is useful as an independent check. The analysis also provides information regarding the nature of the components of the exhaust, which may be useful in the design and development of combustion chambers.

Accurate analysis of exhaust gases from gas turbine combustion chambers is difficult because the fuel is burned with so much excess air that the concentration of the products of combustion is very low. Because of this dilution the more common methods of analysis, such as that employed in Orsat instruments, have proved unreliable. Gravimetric methods of analysis are known to afford precise results when dealing with small quantities, and it appeared that such methods could be applied to the problem of analysis of exhaust gas from combustion chambers for gas turbines. Jordan and Eckman [1][2] used gravimetric methods for the determination of gases in metals. The application to analysis of exhaust gas would depend on efficient separation of the prod-

[1] The work described in this report was sponsored by the Bureau of Aeronautics, Department of the Navy.

[2] Figures in brackets indicate the literature references at the end of this paper.