II are computed on the alcohol-benzene extractive-free basis. The wood acid mixture was diluted according to the Forest Products Laboratory's technic (*1*) and, after refluxing and settling, the supernatant liquid and residue were transferred directly to the crucibles and filter papers. The yields of lignin recorded in Table II indicate that the two methods of filtration give comparable results when applied to the same sample, and that hence either may be used as convenience dictates.

Literature Cited

(1) Bray, *Paper Trade J.*, **87**, No. 25, 59 (1928).
(2) Fuchs, "Die Chemie des Lignins," p. 69, Springer, 1926.
(3) Ross and Hill, *Pulp Paper Mag. Can.*, **27**, 541 (1929).

Table II—Lignin from Same Sample Using Two Different Methods of Filtration

Species	Lignin by Forest Products Lab. Method	Lignin by Matched Filter Paper Method
	%	%
Beech	26.08	25.85
(*Fagus grandifolia* Ehrh.)	26.50	25.70
Basswood	20.10	20.44
(*Tilia glabra* Vent.)	20.13	20.70
Red spruce	28.38	28.54
(*Picea rubra* Link.)	28.36	.....
White pine	27.95	27.99
(*Pinus strobus* L.)	27.91	27.93

Moisture Content of Liquid Sulfur Dioxide[1]

A. K. Scribner

Virginia Smelting Company, West Norfolk, Va.

The ever-increasing use of liquid sulfur dioxide by the electrical refrigeration industry has created wide interest in suitable methods for determining the traces of moisture found in this product. The procedure to be described is rapid, uses a minimum sample, will produce consistent results in any laboratory, and has been in actual plant control work for several years.

The specifications for liquid sulfur dioxide suitable for refrigeration once called for moisture below 200 p. p. m. but today all manufacturing guarantees are below 50, and the actual water content will reach 5 p. p. m. in much of the material shipped. The total evaporation of 146 grams of sulfur dioxide containing 200 p. p. m. of water leaves a residue visible but difficult to estimate. Above this point the water residue increases steadily and can be measured in the tips of the tubes shown in Figure 1.

Table I contains data on the fractionation of wet sulfur dioxide boiling at normal pressure and temperature and furnishes a basis for determining the total moisture content of this sulfur dioxide. (Evaporate a 146-gram sample, record the residue, and refer to Table I.)

Table I—Fractionation of Boiling Sulfur Dioxide[a]
(Sample of sulfur dioxide taken, 146 grams)

(*A*) Moisture as Residue on Evaporation	(*B*) Moisture as Residue Figured on Sample[b]	(*C*) Moisture Figured on P_2O_5 Gain on Evaporation	(*D*) Total Moisture
Ml.	%	%	%
0.005	0.003	0.022	0.025
0.010	0.007	0.023	0.030
0.015	0.010	0.024	0.034
0.020	0.013	0.025	0.038
0.04	0.027	0.027	0.054
0.06	0.040	0.030	0.070
0.08	0.053	0.034	0.087
0.10	0.067	0.038	0.105
0.40	0.267	0.070	0.337

$$\frac{A \times 1}{146} + \frac{P_2O_5 \text{ gain in grams}}{146} \times 100 = \text{total \% moisture}$$

or

$$B + C = D$$

[a] Water above 250 p. p. m.

[b] $\frac{A \times 1}{146} \times 100 = B.$

The inability to see residual water in the moisture tubes has often led to the statement that the sulfur dioxide in question was anhydrous. Chemical tests indicate that this liquid sulfur dioxide contains water, but that the amount of water going off with the sulfur dioxide vapor phase is an increasingly large percentage of the total water. The residue is difficult to determine, but its presence can be detected by the use of the blade test.

A bright piece of low-carbon Swedish steel placed in a sample of boiling sulfur dioxide of 200 p. p. m. water content remains bright during the evaporation, and does not tarnish until the last traces of liquid sulfur dioxide are evaporated. At this point, the blade gives evidence of considerable corrosion, pointing to a concentrated sulfurous acid, which we know is intensely active. The intensity of corrosion, as shown by the etching of the steel, decreases to a point at which the regular P_2O_5 analysis gives 65 p. p. m. Below this point the steel remains bright throughout the entire test.

This test is useful for non-quantitative reports of moisture stating that the sulfur dioxide contains "more than," or "less than" 65 p. p. m. of water.

Possible Methods

An actual determination of the water below 65 p. p. m. calls for an accurate method. Several have been tried.

The specific conductance of the liquid phase can be determined and specifications written on this basis, but the test is difficult and has not yet been developed for practical use in plant control work.

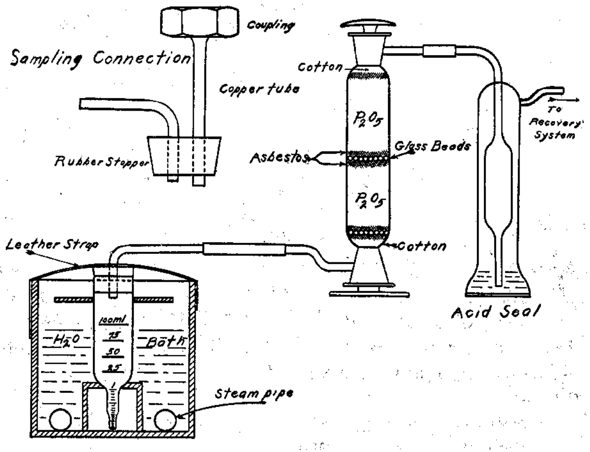

Figure 1—Apparatus for Moisture Determination

An Engelhard cell was used in an endeavor to obtain a moisture curve from the differences in the thermal conductivity of the vapor phase rising from a boiling sample of sulfur dioxide. This method failed.

The color change of a chemical added to boiling sulfur

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[1] Received February 6, 1931.

dioxide would be the ideal procedure, but up to the present time nothing worth while has been developed.

Rapid evaporation of samples with the vapor passing over desiccating agents such as anhydrone, dehydrite, and especially prepared aluminum oxide, was unsatisfactory. Phosphorus pentoxide proved to be the only satisfactory desiccating agent, and is the one now used in this laboratory.

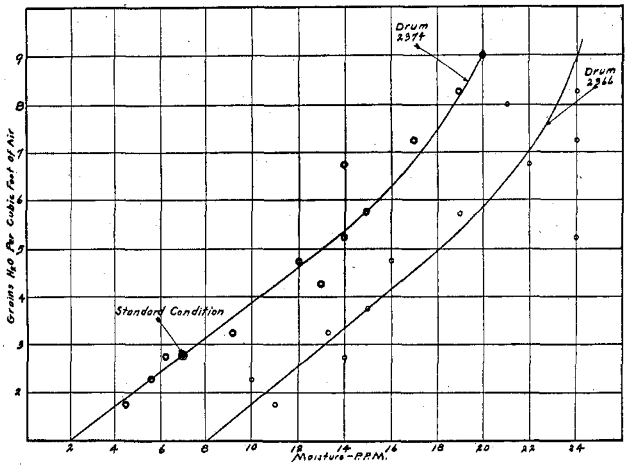

Figure 2—Barometer Drum Tests *vs.* Grains of Water per Cubic Foot of Air

The following method for plant control work is based on a demand for reliable data within 1¹/₂ hours after the sample is taken, and a production of 100 or more analyses daily.

Equipment

The equipment consists of copper sampling connections, especially built Fleming jars packed with P_2O_5-asbestos mixtures, sulfuric acid guide bottles or seals, and moisture tubes graduated as shown in Figure 1. These tubes have a volumetric capacity of 200 ml., but the sulfur dioxide sample consists of 100 ml. or 146 grams.

Procedure

The samples originate from the plant and from shipping containers which have a variable capacity of from 5 to 40,000 pounds (2.27 to 18,144 kg.). Each container is tested. Groups of ten samples are usually taken, and transported in an insulated box to the laboratory, the sulfur dioxide being at 14° F. (−10° C.).

Before sampling, 10 Fleming P_2O_5 jars, already in service, are standardized by the passage of 50 grams of sulfur dioxide. Freshly packed jars should always be standardized by the passage of 500 ml. of sulfur-dioxide gas. Before closing the stopcocks, the jars are vented to the air for 3 seconds, because the speed of evaporation may build up as high as 4 inches (10.16 cm.) of mercury pressure.

At the time of closing the stopcocks, the temperature humidity, and barometer are always recorded. The jars are wiped by passing a dry cloth over them gently, and then weighed, using calibrated weights. The jars are now placed in their racks, ready for the test.

The sample to be analyzed is drawn into a dry, clean moisture tube through the special copper connection. Before sampling, the container valve is blown off, and is then dried, with its sampling device, by a blow torch. The withdrawal of 146 grams of sulfur dioxide requires a few seconds, but the total used for a double check test averages 1¹/₂ pounds (0.680 kg.) per container.

The moisture tubes on reaching the laboratory are hooked up one by one to the closed P_2O_5 jars. This is possible because the sulfur dioxide at 14° F. (−10° C.) in the frosted moisture tubes creates almost no pressure. As each moisture tube is placed on the line, the bottom and top stopcocks of the jars are successively opened, and the rate of flow is measured by bubble formation in the acid seal.

The vapor formation and duration of the tests are controlled by a water bath. The sulfur dioxide flow is maintained at a constant rate during the 60-minute period of the test by gradually elevating the temperature of the water bath as the evaporation proceeds. Leather straps hold the stoppers in the moisture tubes.

On completion of the evaporation, the jars are brought to atmospheric pressure and closed. All conditions are recorded, the jars are wiped in exactly the same manner as before, weighed, and placed in position for the next test that follows immediately.

Moisture tubes are also checked for residue, but sulfur dioxide suitable for refrigeration is water-white, and should leave no residue, oil, or water on evaporation.

PROXIMATE CALCULATION

$$\frac{\text{Grams gain by } P_2O_5}{146} \times 100 = \%\ H_2O \text{ in } SO_2;\ \text{all conditions constant}$$

Correction for temperature change during test period:
- Add 1.3 p. p. m. for each ° F. rise
- Subtract 1.3 p. p. m. for each ° F. fall

Correction for barometer change during test period:
- Add 1 p. p. m. for each mm. rise
- Subtract 1 p. p. m. for each mm. fall

Discussion

The correction factors just described are important and will be explained in more detail, because in this work our average P_2O_5 gain is small. On a 10 p. p. m. average the gain is only 15 mg. on the 146-gram sample.

The Fleming jars, when properly packed with the P_2O_5 asbestos and beads, have voids equivalent to 59 per cent of their total cubical content, which is 0.1025 gram of sulfur dioxide. A difference in temperature between the start and finish of the test will vary this sulfur dioxide content of the P_2O_5 jar enough to influence results. In fact, a variation of 1° F. will give an error in analysis of 1.3 p. p. m.

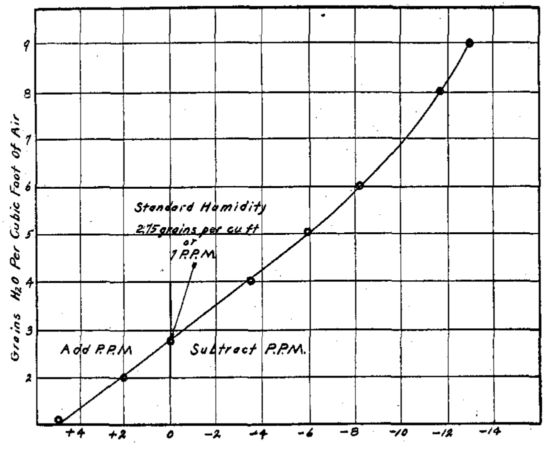

Figure 3—Correction Curve for Standard Conditions

It is difficult in most laboratories to have constant temperature, so the above adjustment should be made for temperature changes.

The inlet and outlet tubes on the standard P_2O_5 jars have a volumetric capacity of 1 ml., which is 0.0029 gram of sulfur dioxide. If the sulfur dioxide is replaced by air, the loss in weight would be 0.0016 gram, or an error of 10 p. p. m. in the test. Therefore, all jars not air-flushed should be weighed quickly after the test. Standing in desiccators will cause deviations, and to avoid this, the jars used call for inlet and outlet capacities of only 0.25 ml.

Barometric changes will affect ultimate results. For instance, a rise or fall of 10 mm. will give a change of 0.0015 gram in the sulfur dioxide capacity of the jar. This is 10 p. p. m., or 100 per cent error. By working in a 60-minute period, deviations from this source are avoided.

Large samples of 500 to 1500 grams of sulfur dioxide evaporated over periods of 5 to 24 hours checked the 60-minute samples within 15 per cent, thus justifying the use of a quick method for control work.

Moisture tubes and other sampling flasks were flushed with dry sulfur dioxide, washed with liquid sulfur dioxide, and then used for the analytical sample. In these cases, the results checked standard analyses taken when the moisture tubes were merely wiped carefully with a warm cloth and kept in an oven between tests.

Blank Test

Variations in analyses made at different seasons of the year and by widely scattered laboratories led to a daily test of one 2000-pound (907-kg.) container called the barometer drum. The actual moisture content of this liquid sulfur dioxide could not alter, but the moisture content as reported by the laboratory varied from time to time. In warm weather, the apparent p. p. m. rose, but on cool, dry days, they decreased. This variation in moisture content was always accompanied by an atmospheric change—namely, the grains of moisture per cubic foot of air. The maximum average month at West Norfolk was June, with 7.5 grains, and the minimum average was December, with 2.5 grains. The daily maximum was 9, and the daily minimum was 0.6.

For 18 months, tests were made on this so-called barometer drum, or blank. The results figured in p. p. m. were plotted against the grains of moisture per cubic foot of air, and produced the curve shown in Figure 2. Several hundred subsequent tests have checked the correctness of this curve as applied to the analytical procedure just described.

The adjustment of all tests to standard conditions is made easy by the correction curve, Figure 3. This is based on a standard of 2.75 grains and 7 p. p. m. for the blank test. The moisture content of samples taken in groups with the blank reflect the variations shown by Figures 2 and 3. Therefore, any test with known humidity can be corrected to standard conditions. When the grains are above 2.75, a minus correction in p. p. m. is applied to the proximate analysis. Below 2.75, a plus correction is used.

ULTIMATE CALCULATION

P. p. m. in proximate analysis ± p. p. m. correction = ultimate analysis

Example—Proximate result = 15 p. p. m.
Grains per cu. ft. = 4.55
Correction = −5
Ultimate analysis = 10 p. p. m.

Conclusion

Elaborate equipment and methods of analysis with absolutely constant conditions the entire year should enable one to obtain check tests day by day. Small laboratories interested in the moisture content of sulfur dioxide do not have the facilities, the extensive technical control, and the equipment for this work. They can, however, follow the method just described and use the correction curve shown in Figure 3 to place their results on a standard basis for comparison.

Acknowledgment

W. F. Pond, M. L. Harris, and B. E. Yaffey, of the staff of this laboratory, assisted in the development and perfection of this method.

Quantitative Separation of Copper and Cadmium by Reduction of Their Salts with Potassium Formate[1,2]

Ellis I. Fulmer

DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE, AMES, IOWA

THIS work grew from observations upon the effect of heat on the formates of several metals. Copper formate when heated gave off metallic copper in such a state of subdivision that the metal came from the mouth of the test tube in a heavy copper-colored vapor. Lead formate yielded metallic lead; zinc formate, the oxide; cadmium formate, the metal and some carbonate. It was very apparent that the temperatures required for these reductions varied greatly with the metal concerned. Hence experiments were instituted to apply this temperature differential to the separation of copper and cadmium.

The heating of the formates of these metals for 2$^1/_2$ hours at 150° C. effected a separation. However, this did not constitute a satisfactory quantitative method because of the powdery nature of the copper and the presence of varying amounts of cuprous carbonate formed.

The next reagent studied was sodium formate. The solution of the sulfates of copper and cadmium was made acid with formic acid and about 15 grams of sodium formate were added to each sample and the solution evaporated to dryness. The samples were placed in an oven at 130° C. for 1 hour. The residue, after cooling, was extracted with hot water. The undissolved material consisted of a mixture of metallic copper and cuprous carbonate. The filtrate was free from copper and an analysis showed all the cadmium to be present in the filtrate. The filtrate was evaporated to dryness and again placed in the oven. There was no reduction of cadmium salt until 145° C. had been reached.

Experiments with potassium formate showed several differences between this reagent and the sodium salt, which may be summarized as follows:

REAGENT	MIXTURE FUSES ° C.	COPPER SALT REDUCED ° C.	CADMIUM SALT REDUCED ° C.
Sodium formate	250	135 to 140	145 to 150
Potassium formate	150	100	200

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[1] Received February 7, 1931.

[2] This material is taken from a thesis submitted by the author for the degree of master of arts at the University of Nebraska in 1913. The author feels that the material here summarized is interesting not only for the separation involved but in calling special attention to potassium formate as a reagent of more general applicability. Permission has been given by F. W. Upson of the University of Nebraska for the publication of the material in its present form. The author wishes to thank Benton W. Dales for advice during the progress of the work.