successfully in the determination of other radioactive substances in small quantity for scientific purposes; but since it is the object of the present paper to deal only with the practical methods of measuring radium itself, they do not require consideration here.

THE GAMMA-RAY METHOD OF MEASURING RADIUM

Radium itself emits α -rays only, but both RaB and RaC emit γ -rays which present the most convenient means of measuring radium in quantities above 0.1 mg. and of not less than 0.05 per cent purity. Since RaB and RaC are products resulting from the decay of radium emanation, a gas, it is necessary to confine radium preparations in a closed vessel to prevent the escape of gas before the measurement is made. The measurement may be carried out after the vessel has been closed for a month or more, in which case the γ -radiation will have reached a constant maximum and no time correction will be necessary; the γ -radiation then having become directly proportional to the quantity of radium present, as is the case of all standard tubes of radium salt which have been sealed for more than a month. If the measurement is made prior to this period, a correction must be made for the unelapsed time. This correction is readily made by reference to the Kolowrat table, just as described in Part II¹ for the emanation method.

FIG. 3

In order that the accumulation of emanation shall have taken place over a definite period of time, the starting point must be rendered exact by sealing the radium salt in a glass tube as soon after crystallization as possible. It is first necessary, however, to dry the salt thoroughly by raising the temperature for 20 min. or more to 250° C. or higher. Otherwise, decomposition by the α -rays of any water remaining, even in the form of water of crystallization, would generate a dangerous gas pressure in the limited volume of the tube. If the zero period is indefinite or not known, a series of measurements must be made at different intervals, from which the final maximum value can be calculated by comparisons with the Kolowrat table.

The measurement itself consists simply of a comparison of the rates of discharge produced by a tube with known radium content and that of the unknown, each being placed successively in the same fixed position at a suitable distance from the discharge chamber. Almost any type of electro-scope may be used by placing a lead screen, one-eighth to one-

fourth inch thick, between the instrument and the tube containing the radium. A type of γ -ray electro-scope is shown in Fig. 3.

An accuracy of about 1 per cent can be readily attained with ordinary precautions by the use of the simple aluminum or gold-leaf electro-scope.

Radium salts are bought and sold in the United States almost entirely on the certificate of the Bureau of Standards. The measurements are made electroscopically by the γ -ray method, using standards that have been compared with the International standard in Paris. Every radium laboratory should have at least one secondary standard that has been certified by the Bureau of Standards.

Radium emanation, which is now quite largely used therapeutically instead of radium itself, may be measured by the γ -ray method exactly as radium, and is expressed in equivalent units, one curie being the amount of emanation in equilibrium with one gram of radium element. It is necessary only to allow the emanation to remain in a closed vessel for 4 hrs. to arrive at maximum γ -radiation before making the measurement. In making this measurement, one additional correction is necessary. On account of the short life of radium emanation (3.85 days half period) RaC lags behind in decaying by 0.8 per cent; and since it is RaC, not emanation, which furnishes the principal γ -rays, this correction must be deducted from the γ -ray indication to give the true quantity of emanation. If one wishes to know simply the γ -radiation and not the actual quantity of radium emanation, this correction is not necessary.

The writer is indebted to the Denver Fire Clay Company for Figs. 2 and 3, and to the Sachs-Lawlor Company of Denver for permission to describe Mr. Elzi's arrangement shown in Fig. 1. The electroscopes described are made by the Sachs-Lawlor Company and distributed by the Denver Fire Clay Company.

THE DISTRIBUTION OF CERTAIN CHEMICAL CONSTANTS OF WOOD OVER ITS PROXIMATE CONSTITUENTS

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INTRODUCTORY

In a previous paper,¹ the author has proposed a scheme for separating wood into a number of proximate groups. In addition to the groups designated, certain organic radicals (such as CH_3O and CH_2CO) are known to occur in woods. Any given species is characterized by definite contents of these radicals which have accordingly become quite generally recognized as constants for that particular wood. They found no place in the proposed scheme for the reason that the quantitative relations between these so-called constants and the proximate groups were not known and it appeared likely that their inclusion would produce an overlapping of constituents. The purpose of

¹ Loc. cit.

¹ THIS JOURNAL, 11 (1919), 556.

the present investigation has been to learn the relations existing between the more important constants and proximate groups. Experiments have, therefore, been conducted to ascertain the distribution of (1) furfural-yielding groups, (2) acetic-yielding groups, and (3) methoxy groups, over the two chief proximate groups—cellulose and lignin.

The three above-mentioned constants have been considerably investigated. The pioneer work of DeChalmot¹ on the furfural-yielding complex and of Benedikt and Bamberger² on the methoxy groups has resulted in quantitative data for the most important woods and fibrous products and considerable information as to the relation of these data to the life history of the plant. Cross and Bevan³ have studied the production of acetic acid from the lignocelluloses by various reactions of decomposition. Of these reactions, acid hydrolysis may probably be safely taken as a measure of the acetic-yielding groups preëxistent in the woods, which according to these authors are not acetyl groups, CH_3CO , but acetic residue groups CH_2CO .⁴ Schorger⁵ has recently reported values for all three of these constants for a number of American woods.

The yields of acetic acid by hydrolysis and methoxy groups by the Zeisel method have a considerable industrial significance as measures, respectively, of the maximum commercial yields of acetic acid and wood alcohol obtainable by destructive distillation. The fact that the full yield of these substances is never realized industrially, due to losses by secondary reactions,⁶ detracts from the practical value of their determination. On the other hand, it affords an incentive for the improvement of the manufacturing processes in the direction of a closer approach to theoretical yields. The furfural yield is not a measure of valuable products in the wood, but its determination in finished products has been used to give information as to the source of raw materials used in their manufacture.⁷

While precise information is lacking as to the relation of these constants to cellulose and lignin, certain opinions have found considerable support. The methoxy group is generally recognized as being closely connected with the lignin complex and the methoxy determination has been proposed as a measure of the lignin content.⁸ The furfural-yielding groups have been found to be partly associated with the cellulose and partly with the lignin. W. E. Cross⁹ has concluded from his experiments that the groups yielding acetic acid by hydrolysis are contained in the lignin and absent from the cellulose portion of woods.

The extent to which any of these radicals remain attached to either the cellulose or lignin, when lignocellulose is subjected to reactions of decomposition,

must necessarily depend very much upon the nature and intensity of these reactions. The experiments herein described were conducted to ascertain the distribution of the constants under certain specified conditions, namely, those of the analytical determinations of cellulose and lignin. The results may therefore be taken to indicate whether the constants are to be regarded as groupings attached to and subordinate to these chief proximate groups, or as possessing an independent existence and themselves entitled to rank as proximate groups.

EXPERIMENTAL

The experiments were confined to redwood (*Sequoia sempervirens*). A quantity of sawdust was obtained by making a number of cross-sectional cuts through a redwood slab. The mixture of coarse and fine sawdust was sifted through a 50-mesh screen and the selected fine material used for the various determinations. The samples were analyzed in the air-dry condition with a moisture content of 11.62 per cent.

PREPARATION OF EXTRACTED WOOD—Portions of 2 g. were weighed into alundum thimbles and extracted in a Soxhlet apparatus for 6 hrs. with benzene, then for a further 6 hrs. with 95 per cent alcohol. The substance was then transferred to Gooch crucibles, containing as a filtering medium disks of mercerized cotton cloth, and washed with distilled water. Material so prepared is regarded as purified lignocellulose free from extractives.

PREPARATION OF CELLULOSE—Two grams of the wood, extracted as above, were subjected to the alternate action of chlorine and hot 3 per cent sodium sulfite solution in accordance with the procedure of Sieber and Walter.¹ The moistened material was placed in a Gooch crucible and the gas drawn through it by suction for 4 periods of 20, 15, 15, and 10 min. After each chlorination the residue was treated with half saturated sulfurous acid, washed with hot water, digested in 3 per cent sodium sulfite solution for 45 min., filtered off, and washed thoroughly with hot water. After the final treatment the residue was dried for 16 hrs. at 100° C.

PREPARATION OF LIGNIN—Two grams of the wood were extracted as before, partly dried at 60° C. and placed in a 750 cc. Erlenmeyer flask. 20 cc. of 72 per cent sulfuric acid were added and the flask rotated so as to bring all parts of the sawdust in contact with the acid. It was then allowed to stand 3.5 hrs. Fifty cc. of cold water were added, followed by 500 cc. of hot water, the mixture filtered on a Gooch crucible containing a cloth filtering disk, washed and dried for 16 hrs. at 100° C.

ANALYTICAL METHODS FOR DETERMINING THE CONSTANTS

FURFURAL-YIELDING GROUPS—These were determined by distillation of the material with 12 per cent hydrochloric acid (sp. gr. 1.06) and precipitation of the furfural in the distillate with phloroglucine, according to the method described by Schorger for pentosans.² No correction was made for methyl furfural, the total precipitate being calculated to furfural.

¹ *Papier-Fabr.*, 11, 1179; *Chem. Abs.*, 8 (1914), 1202.

² *THIS JOURNAL*, 9 (1917), 558.

¹ *Am. Chem. J.*, 16 (1894), 218; Cross and Bevan, "Cellulose," p. 181.

² *Monatsh.*, 11 (1890), 260; "Cellulose," p. 188.

³ "Cellulose," p. 191.

⁴ Cross and Bevan, "Researches on Cellulose," 3, 103.

⁵ *THIS JOURNAL*, 9 (1917), 560.

⁶ Palmer, *Ibid.*, 7 (1915), 633; Schorger, *Ibid.*, 9 (1917), 556.

⁷ Tollens, *J. Soc. Chem. Ind.*, 26 (1907), 987.

⁸ Benedikt and Bamberger, *Loc. cit.*

⁹ *Ber.*, 43, 1526.

ACETIC-YIELDING GROUPS—The material was hydrolyzed by heating for 3 hrs. under a water-cooled reflux condenser with 100 cc. of 2.5 per cent sulfuric acid. The mixture was quickly filtered into a 750 cc. flask to avoid the introduction of carbon dioxide and washed with CO_2 -free water to a total volume of about 200 cc. The acetic acid in the solution was then distilled off and determined by means of the following apparatus:

The 750 cc. flask was placed in a paraffin bath and closed by a rubber stopper containing a glass stop-cocked funnel tube and a delivery tube. The funnel tube served to introduce CO_2 -free water during the distillation and was protected by a soda lime tube attached to its open end by means of a rubber stopper. The delivery tube bent downward and terminated in a vertical condenser. This in turn was connected by a rubber stopper to a suction filter flask which served as a receiver for the distillate.

Suction was applied to the receiver and the paraffin bath raised to and maintained at 85°C . Higher temperatures were avoided as tending to the formation of formic acid from the hexose carbohydrates present. When most of the liquid had distilled over from the flask, 100 cc. of CO_2 -free water were introduced and distilled over, after which the procedure was repeated with a second 100 cc. The total distillate was then removed and titrated with standard sodium hydroxide solution using phenolphthalein as indicator. The results, representing "total volatile acids," were expressed as acetic acid.

To obtain the actual acetic acid it was necessary to correct for the formic acid invariably present. A few cc. of silver nitrate solution were added to the solution after titration and the mixture left upon the steam bath for several hours. The silver formate was thereby decomposed, yielding an amount of metallic silver corresponding to the formic acid present. The precipitated silver was filtered off, washed, dissolved in dilute nitric acid, precipitated as silver chloride, filtered off, washed, ignited, and weighed. From the weight of silver chloride so obtained the amount of acetic acid equivalent to the formic acid was calculated by multiplying by the conversion factor 0.4. This result, deducted from the total acidity as found above, gave the actual acetic acid present.

METHOXY GROUPS—Methoxy groups were determined by the Zeisel method.¹ The apparatus and procedure here described have been found to give consistent results.

The decomposition flask was a small distillation flask (of about 130 cc. capacity) having its side tube connected with a carbon dioxide generator. In the mouth of the flask was placed a perforated cork carrying a delivery tube. This delivery tube ran vertically for 50 cm. and so acted to some extent as a reflux condenser and fractionating column. It then made two right-angled bends and, descending, was connected at its lower extremity with two U-tubes in series. The first of these contained distilled water and a few milligrams of phosphorus, the second distilled water only.

¹ *Monatsh.*, 6 (1885), 989; Meyer-Tingle, "Determination of Radicals in Carbon Compounds," John Wiley & Sons, Inc., p. 38.

The U-tubes were placed in a beaker of water arranged to be heated by a Bunsen burner. From the second U-tube, a delivery tube ran to the absorption apparatus which consisted of an Erlenmeyer flask and a Fresenius nitrogen bulb. The general arrangement and dimensions of the apparatus are shown in the accompanying figure. The paraffin and water baths and the carbon dioxide generator are omitted.

In the first and second absorption flasks were placed 35 and 15 cc., respectively, of freshly filtered alcoholic silver nitrate solution. (The solution was prepared by dissolving 10 g. of solid silver nitrate in 25 cc. of water and adding 225 cc. of 95 per cent alcohol.) 0.3 g. of material was placed in the decomposition flask and 15 cc. of hydriodic acid (1.70 sp. gr.) were added. The mixture was heated to 130°C . on a paraffin bath and the temperature maintained at 130° to 140°C ., while a slow stream of carbon dioxide was passed through the apparatus. The beaker of water surrounding the U-tubes was kept at a temperature of 50° to 60°C . throughout the process. The operation was continued until the precipitated silver iodide in the absorption apparatus settled out, leaving a clear supernatant liquid, indicating the completion of the reaction.

The apparatus was then disconnected and the contents of the absorption flasks rinsed into a 600 cc. beaker. Water sufficient to make about 500 cc. was added and the whole evaporated on the steam bath to a volume of 150 to 200 cc. in order to expel the

alcohol. A few drops of nitric acid were added, the solution again diluted to about 500 cc. and allowed to stand on the steam bath for about one-half hour for the silver iodide to settle. The precipitate was then collected in a tared asbestos Gooch crucible, washed, dried at 130° C. for 2 hrs., and weighed. CH_3O was calculated from the weight of silver iodide by multiplying by the factor 0.132.

By the above methods the furfural yield, acetic yield on hydrolysis, and methoxy yield were determined upon the raw wood, extracted wood, cellulose, and lignin. The results are shown in the table.

DISTRIBUTION OF GROUPINGS IN REDWOOD
Expressed in Percentages of Air-Dried Wood (11.62 Per cent Moisture)

	Furfural Yield	Total Volatile Acids by Hydroly- sis	Formic Acid Expressed as Acetic	Actual Acetic Acid by Difference	Methoxy Group
Raw Wood.....	5.73	0.94	0.16	0.78	5.46
	5.95	1.03	0.16	0.87	5.74
AVERAGE.....	5.84			0.83	5.60
Extracted Wood.....	5.77	0.75	0.09	0.66	5.33
	5.65	1.03	0.06	0.97	5.35
AVERAGE.....	5.71			0.82	5.34
Cellulose.....	2.36	0.75	0.21	0.54	0.35
	2.69	0.66	0.10	0.56	
AVERAGE.....	2.52			0.55	0.35
Lignin.....	0.24	0.09		0.09	5.49
	0.23	0.09		0.09	5.78
AVERAGE.....	0.24			0.09	5.63

Determinations were also made of the furfural yield of the filtrates and washings from the cellulose determination. The combined solutions from four determinations or 8 g. of wood were evaporated to somewhat less than 500 cc., placed in a 500 cc. volumetric flask, and diluted to the mark. 1.25 cc. aliquots corresponding to 2 g. of original wood were placed in the distilling flasks and mixed with 30 cc. of concentrated hydrochloric acid. The determination was then carried out as usual. Three determinations gave 2.30, 2.08, and 2.08 per cent of furfural in the chlorination liquors, the results being referred to the weight of air-dried wood.

Determinations of the methoxy group were made upon portions of lignin that had been hydrolyzed by boiling with 2.5 per cent sulfuric acid for 3 hrs. after being separated by the usual treatment with 72 per cent sulfuric acid. The methoxy content based on the original wood was 4.08 and 3.88 per cent. There is accordingly an average loss of 1.65 per cent of methoxy during the hydrolysis. Separate experiments have shown that the weight of lignin after the treatment is about 2 per cent less than when prepared in the usual manner. From the above results it is evident that the loss in weight of lignin is due chiefly to the splitting off of the methoxy group.

DISCUSSION

The foregoing results indicate that none of the three radicals investigated is to be regarded as existing entirely independent of the proximate constituents cellulose and lignin. Apparently they are so related to these substances that, when lignocellulose is attacked by hydrolytic reactions, they tend to remain at least partially joined to the cellulose or the lignin or to both.

No method is known whereby lignocellulose may be separated so as to yield both cellulose and lignin unchanged, but in every case one of them is obtained as a residue while the other is converted into alteration products and removed. It is therefore unsafe to draw

the conclusion that radicals found with either cellulose or lignin, or both, exist similarly associated with them in the original lignocellulose complex. The radical is rather to be regarded as occupying an intermediate position between these chief proximate constituents, and remaining with the residue according to the extent that it resists the treatment employed. The same portion that remains with the cellulose under the conditions of one type of decomposition may remain with the lignin under another set of conditions.

A comparison of the data for raw and extracted wood shows that none of the three constants examined is materially affected by treatment with non-hydrolyzing solvents.

About half of the furfural-yielding complex remains in the cellulose residue. Most of the remaining portion is found in the chlorination liquors. As was pointed out in a previous paper¹ this last portion is probably due to xylan or other true pentosan existing as such in the wood, while the non-hydrolyzable furfural-yielding material contained in the cellulose is probably oxycellulose. The amount of furfural-yielding material remaining with the lignin is almost negligible.

The amount of acetic acid present in redwood is small and its determination is rendered uncertain by the presence of formic acid either preëxisting or produced by the action of the hydrolyzing acid upon hexoses. No general conclusions can therefore be drawn in regard to its distribution but it appears to be associated chiefly with the cellulose constituent. With the lignin there is very little. The combined amount found with the lignin and cellulose is slightly less than the total amount in the wood, indicating that part of the acetic-yielding groups separates independently. In view of the small quantities involved the results are not conclusive. In the case of redwood, and probably also in the case of other coniferous woods, which yield only small amounts of acetic acid on hydrolysis, it would appear that acetic acid should not be considered as an independent proximate group but as a radical already largely accounted for in the cellulose and lignin residues. This conclusion probably does not apply to hardwoods, where the acetic yield is much higher.

The methoxy groups are found quantitatively in the lignin constituent, directly confirming the frequent assertion that methoxy is a purely lignin characteristic. This occurs only when lignin is separated by the method described and subsequent hydrolysis avoided. If this is not done there is considerable splitting off of the methoxy groups.

These facts have an important bearing upon the proximate analysis of wood. A summative analysis of a wood may be made by drying, extracting with benzene and alcohol, and determining the cellulose and lignin in the manner previously described. It appears from the foregoing results that, when this is done, the cellulose and lignin constituents account for all of the methoxy group, nearly all of the acetic-yielding groups, and about half of the furfural-yielding groups. Except for the furfural due to hydrolyzable pentosans found

¹ Dore, *THIS JOURNAL*, 12 (1920), 264.

in the chlorination washings, these constants are not to be regarded as proximate constituents but rather as radicals connected with the constituents cellulose and lignin. With the exception noted, these constants may be ignored in the summative analysis of coniferous woods.

SUMMARY

I—A study is made of the distribution of the groups contained in redwood which yield furfural, acetic acid, and methoxy, with the object of learning their relation to the constituents cellulose and lignin.

II—About half of the furfural-yielding groups are associated with the cellulose, but only a small amount with the lignin. The portion present as true pentosan is hydrolyzed and removed during chlorination.

III—The acetic-yielding groups are partly associated with the cellulose, much less so with the lignin. A small amount appears to be detached from either. The results are not conclusive in view of the small amount present in redwood and the analytical difficulties. In the case of coniferous woods acetic acid probably need not be considered as a proximate group.

IV—The methoxy groups are wholly associated with the lignin. They may be partially split off from it by acid hydrolysis.

V—In the summative analysis of coniferous woods, all of the acetic-yielding and methoxy groups and part of the furfural-yielding groups may be disregarded as already accounted for in the cellulose and lignin. The furfural-yielding substances contained in the chlorination washings and representing hydrolyzed pentosans should be estimated.

THE PROXIMATE ANALYSIS OF CONIFEROUS WOODS

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INTRODUCTORY

A method has been recently proposed by the author for the summative proximate analysis of woods.^{1*} Later investigations have shown the advisability of certain modifications of the original scheme which are considered in detail in this paper.

The proposed system for the analysis of wood effected a separation of the wood substance into the following fractions: loss on drying, benzene extract, alcohol extract, water-soluble, soluble in one per cent sodium hydroxide, cellulose, and lignin. Full information as to the composition of these fractions was lacking, but it was believed that the wood constituents were separated into logical groups based upon chemical similarity and economic value.

The scheme was found to account for nearly all of the material of coniferous woods in that the sum of all constituents varied from 96 to 97 per cent for the three conifers examined. With the hardwoods the method was unsuccessful, as 10 to 17 per cent of the constituents remained unaccounted for. The available data seem to indicate that the chemistry of the hardwoods is an entirely separate problem. The woods of the broad-leaved trees have accordingly been omitted

from consideration in this investigation and the conclusions are applicable to the conifers only.

DEFECTS IN PROPOSED SCHEME

(1) ITS FAILURE TO GIVE CORRECT RESULTS FOR CELLULOSE AND LIGNIN—It was noted in the original paper¹ that when digestion in one per cent sodium hydroxide was used less cellulose and lignin were obtained than when this treatment was omitted. In a subsequent paper² it was shown that the diminished yield of cellulose was due to partial destruction of true cellulose instead of to greater purity of the product. Accordingly the results for cellulose are incorrect. No direct data are available for lignin, but it has been shown in the preceding paper that lignin readily loses a portion of its methoxy groups when it undergoes acid hydrolysis. Possibly the same effect is produced by alkalis.

(2) THE VAGUE SIGNIFICANCE OF THE WATER-SOLUBLE AND ALKALI-SOLUBLE FRACTIONS—In the absence of detailed studies of the substances contained in these portions, it was believed that they consisted of substances corresponding approximately to König's "proto" and "hemi" forms of cellulose and lignin.³ It is apparent from subsequent studies,² however, that they contain also degradation or hydrolytic products of true cellulose and true lignin. The numerical expression of these fractions has therefore no value as an analytical statement of wood constituents.

(3) THE FAILURE TO EXPRESS THE HEMICELLULOSES—Schorger's studies of mannan⁴ and galactan⁵ have shown that these carbohydrates are found in all conifers, sometimes in considerable quantity. Xylan is well known as a constituent of woods. It is therefore evident that a complete analysis of a wood should take these hemicelluloses into consideration. In the proposed scheme the water- and alkali-soluble portions only partially accounted for these bodies together with other substances.

(4) ORGANIC RADICALS—The original scheme took no account of organic radicals present—the so-called "wood constants." The preceding paper has shown that, with the exception of the furfural-yielding substances soluble in the chlorination washings, these radicals may be disregarded as proximate constituents of coniferous woods.⁶ The original scheme is defective, however, in that it ignores this soluble furfural-yielding substance.

The remedies for the above defects are quite evident. The cellulose and lignin determinations should be made reliable by omission of the alkaline hydrolysis. The water- and alkali-soluble fractions would disappear, leaving the hemicelluloses entirely unaccounted for. It would then be necessary to give the hemicelluloses a separate place in the scheme, and methods would be required for their estimation either collectively or individually. The soluble furfural-yielding substance (probably the pentosan, xylan) would be included in the hemicelluloses.

The present investigation is an attempt to revise the original scheme in accordance with the above suggestions. Methods have been applied for the determination of the hemicelluloses. The revised procedure has then been checked by making these and

* Numbers refer to Reference, page 479.