

0.6788 g. acetyl derivative gave 0.4002 g. acetic acid	Per cent Acetyl	Per cent Calculated for
0.3441 g. acetyl derivative gave 0.2061 g. acetic acid	Acid Found	$C_8H_9O_5(OC.CH_3)_2$
	58.96	$C_8H_7O_5(OC.CH_3)_3$
	59.90	48.78
		62.5
	

The results indicate a mixture of triacetyl derivative with a lower derivative.

(b) *Derivative with Hydrated Sodium Acetate*—The procedure followed in this case was identical with that described above except that 4 g. of crystalline sodium acetate and 10 g. of galactan to 50 g. of acetic anhydride were employed. A yield of 3.5 g. of the purified acetyl derivative was obtained.

Approximately 0.3 g. of the derivative was hydrolyzed by boiling with 100 cc. of $N/4$ H_2SO_4 under a reflux condenser for about 4 hrs., complete solution being obtained. The solution was then titrated with standard alkali in the usual manner.

0.2625 g. acetyl derivative gave 0.1297 g. acetic acid	Per cent Acetyl	Per cent Calculated for
0.3530 g. acetyl derivative gave 0.1722 g. acetic acid	Duplicates	$C_8H_9O_5(OC.CH_3)_2$
	49.78	Mean
	49.40	49.09
		Calculated for
		$C_8H_9O_5(OC.CH_3)_2$
		48.78

The results show that in this case an approximately pure diacetyl derivative of the galactan was obtained.

OCCURRENCE OF GALACTANS IN OTHER CONIFERS

A number of species of conifers were examined to determine if galactans were a normal constituent. Approximately 100 g. of the wood in the form of fine sawdust were extracted several times by digestion with hot water on the steam bath, the aqueous extract evaporated nearly to dryness and the residue treated with 60 cc. of nitric acid in the manner previously described. The crystalline residues obtained were filtered off, washed with water, and dissolved in a minimum amount of boiling water. The solution was filtered hot and the filtrate allowed to stand in the cold for 24 hrs. The mucic acid was then filtered off, washed with water, alcohol, and ether and the melting point determined. Owing to the unreliability of the method of determining galactans quantitative results were not attempted and for the same reason a failure to obtain mucic acid in certain samples is not a positive indication of their absence. The results obtained are given in the following table in which the signs + and — indicate the presence or absence of mucic acid:

Sample No.	SPECIES	Mucic Acid Present	Melting Point Mucic Acid
a	Longleaf Pine (<i>Pinus palustris</i>)	+	214–215°
314-11	Longleaf Pine (<i>Pinus palustris</i>)	+	215
314-12	Longleaf Pine (<i>Pinus palustris</i>)	+	215
314-13	Longleaf Pine (<i>Pinus palustris</i>)	+	210
314-41	Pond Pine (<i>Pinus serotina</i>)	+	210–211
314-31	Cuban Pine (<i>Pinus heterophylla</i>)	+	211
314-35	Cuban Pine (<i>Pinus heterophylla</i>)	+	212
314-21	Loblolly Pine (<i>Pinus taeda</i>)	—	
314-22	Loblolly Pine (<i>Pinus taeda</i>)	+	212
314-30	Loblolly Pine (<i>Pinus taeda</i>)	—	
1	Douglas Fir (<i>Pseudotsuga taxifolia</i>)	+	215

The longleaf and Cuban pines gave apparently the largest amounts of mucic acid.

SUMMARY

I—The wood of the western larch (*Larix occidentalis*) has been found to contain approximately 10 per cent of a galactan not previously described and which has been named ϵ -galactan.

II—The only sugar obtained on hydrolysis of ϵ -galactan is galactose.

III—The determination of galactans by oxidation to mucic acid by the method of Tollens has been shown to be unreliable.

IV—Galactans have been shown to be characteristic of several of the common conifers.

FOREST PRODUCTS LABORATORY, MADISON, WIS.

A MODIFICATION OF WHIPPLE'S METHOD FOR ORGANIC NITROGEN IN SEWAGES

By F. W. BRUCKMILLER AND L. E. JACKSON

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The direct process for total nitrogen in sewages consists in the digestion of a known quantity of sewage in acid solution with or without $CuSO_4$, making decidedly alkaline with $NaOH$, allowing to settle until clear, and nesslerizing an aliquot portion made up to 50 cc. volume. Several methods embodying these principles have been proposed. Their chief point of difference consists in the reagents used to remove such substances as calcium and magnesium, which cause a turbidity upon nesslerization. They are best adapted to that particular sewage for which they were designed. That another factor of equal importance needs some emphasis was forcibly brought home to us upon trying to apply one of the already proposed methods to Kansas sewages; namely, the effect of time the digestates are alkaline before nesslerized, upon the quantity of nitrogen obtained.

HISTORICAL

Rideal¹ was the first to propose a method whereby organic nitrogen could be determined by direct nesslerization. His method is as follows: 10 cc. of a sewage, or 100 cc. of an effluent plus 4 cc. of pure sulfuric acid, are heated in a pear-shaped hard glass flask in a slanting position until the liquid becomes colorless. When about 2 or 3 cc. remain, the flask is cooled and is washed out with small quantities of ammonia-free water into a 100 cc. measuring flask until the volume reaches about 40 cc. An excess, *i. e.*, about 25 cc. of soda solution (25 per cent) free from ammonia is now added, when a flocculent precipitate is thrown down. After cooling, the liquid is made up to 100 cc., transferred to a clean, dry, stoppered bottle, and shaken at intervals until the flocculi subside. A suitable fraction of the clear liquid is then pipetted off into a Nessler glass, diluted to 50 cc., and nesslerized.

McGowan² used a similar method, the chief difference being the addition of potassium oxalate to the alkaline solution to precipitate the calcium, and a proviso that the solution be "rendered just alkaline with purified potash."

Phelps³ used the following method with some success: The sewage is digested with 5 cc. of concentrated H_2SO_4 until colorless, cooled, and diluted to 250 cc. A 2 cc. portion is neutralized with $NaOH$

¹ Sewage, 2nd Ed., 1907, 39.

² 4th Rep. Royal Com. of Sew. Disp., 4, 35, Part 2.

³ J. Infect. Dis., 1 (1904), 327.

(5 per cent), made up to 50 cc., and a portion nesslerized *at once*.

The Columbus Sewage Testing Station¹ published a modification of the Rideal and McGowan methods which is as follows: Measure out an amount of sewage that will contain 0.0005 to 0.001 g. of nitrogen. Add 5 cc. of H₂SO₄, digest until colorless, and rinse the digestate into a 50 cc. flask. Cool and fill to the mark, and pipette 25 cc. into a 100 cc. flask. Add NaOH (250 g. per liter) until a precipitate forms, then add 2 cc. of Na₂CO₃ (100 g. per liter). Mix and make up to volume and allow to stand 6 hrs. Nesslerize 10 cc. made up to 50 cc. in a Nessler tube, reading after 15 min.

L. Whipple² tried to use the Columbus modification on Boston sewage but found that he could not get accurate results, so recommended the following: 50 cc. of the sample are digested with 5 cc. of concentrated sulfuric acid, and a small amount of CuSO₄ until colorless. The digestion is completed by the addition of a few crystals of permanganate to the hot acid. After cooling, the digestate is diluted to 250 cc., mixed, and a portion (25 cc.) is pipetted out and mixed with an equal portion of 5 per cent NaOH, and filtered through a filter paper which has been washed previously with 100 cc. or so of ammonia-free water: 20 cc. of the filtrate are pipetted into a Nessler tube and made up to 50 cc. with water. Mix by pouring one tube into another, and nesslerize. Read after 10 min. A blank should be run on the entire process.

Because of its rapidity, this latter method was tried on Kansas sewages, but with no success, the results obtained always being too low. As we had no trouble due to turbidity in the tubes, we started an investigation to see under what conditions exact results could be secured. For this purpose the effect of large and small amounts of copper sulfate and potassium permanganate were ascertained, as well as the effect of the length of time the samples stood before nesslerizing. The results of our work were finally embodied in the following method which we have found to give accurate results on Kansas sewages at least.

METHOD ADOPTED FOR KANSAS SEWAGES

To 100 cc. of sewage add 5 cc. concentrated H₂SO₄, 2 cc. CuSO₄ (10 per cent) and digest till clear, and then a half hour longer. A small crystal of KMnO₄ is added, and, after cooling, the whole is made up to 250 cc.: 25 cc. are pipetted out into a 100 cc. Nessler tube, 25 cc. of NaOH (5 per cent) added, and the volume made up with ammonia-free water: the tube is then stoppered and allowed to stand 24 hrs.: 10 cc. are nesslerized after making up to 50 cc. The reading on standard $\times 10 =$ parts per million of nitrogen.

EXPERIMENTAL

In all the work the following distillation method as recommended by the Standard Methods of Water Analysis was used to check the direct results: To

¹ *Public Health*, 31, 116, Part 2.

² *San. Research Lab.*, 4, 162.

100 cc. of sewage add 5 cc. of concentrated H₂SO₄ and 10 cc. CuSO₄ (10 per cent), digest until clear, and then a half hour longer. Add 0.5 g. KMnO₄, make up to 500 cc., and pipette 50 cc. into a steam distillation flask. Add 50 cc. Na₂CO₃ (10 per cent) and distil over 250 cc. Make up to 500 cc. and nesslerize 50 cc. Reading $\times 10 =$ parts per million of nitrogen.

EFFECT OF TIME—In the method at first employed, the samples were nesslerized as soon as they had settled clear, or immediately after filtering. A few typical results are given in Table I. Since the results by direct nesslerization were always too low, it occurred to us that an increase of time for the reaction in alkaline solution might increase the amount of nitrogen found. A series of samples of raw sewage were run, allowing the digestates to stand 24 hrs. before nesslerizing. A shorter period did not give good results. A few of the results are found in Table I.

TABLE I—NITROGEN IN PARTS PER MILLION RAW SEWAGE

IMMEDIATE NESSLERIZATION:													
Distillation	25	25	10	85	35	30	35	50	40	25	35	54	48
Direct	17	10	15	14	17	10	7	20	20	14	20	52	34
EFFECT OF TIME:													
Distillation	50	30	40	25	40	35	30	50	30	25	35		
Direct { At once	15	10	20	10	22	18	18	15	14	10	20		
After 24 hrs.	50	20	35	20	38	30	25	50	28	22	35		

EFFECT OF KMnO₄—The fact that in the distillation method we added 0.5 g. KMnO₄ while in the direct we added only a small crystal, suggested to us that in the latter case we might not be adding enough KMnO₄ in order to bring about an equivalent amount of oxidation. Experiments with varying amounts of KMnO₄ in both methods showed that the concentration of the KMnO₄ did not influence the results at all.

EFFECT OF CuSO₄—Varying concentrations of CuSO₄ were tried, and equally as good results were obtained with 2 cc. as with 10 cc. of 10 per cent solution of CuSO₄.

CONCLUSIONS

1—The direct method for determining organic nitrogen in sewages proposed by Whipple has been slightly modified.

2—The length of time the digestates are alkaline influences the accuracy of the results. We found that the best results could be obtained by allowing the samples to stand 24 hrs. before nesslerizing.

3—Increase in concentration of potassium permanganate has no influence on the results obtained.

4—Increase in concentration of copper sulfate has no effect.

WATER AND SEWAGE LABORATORY
UNIVERSITY OF KANSAS, LAWRENCE

ON THE VOLUMETRIC DETERMINATION OF TIN BY POTASSIUM IODATE

By GEORGE S. JAMIESON

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The iodine and ferric chloride methods are the ones most commonly employed for the volumetric estimation of tin. The iodine method is based upon the titration of stannous chloride in hydrochloric acid solution with iodine, using starch as indicator, while the ferric chloride method in general use is based