

Pyridine ( $C_5H_5N$ ) was found by Laurent<sup>1</sup> to be toxic in a one per cent. solution to the fungi which he studied. It has been observed by Falkenburg<sup>2</sup> that the vapor of pyridine and some of its homologues is poisonous to bacteria.

In the experiments with wheat seedlings by Schreiner and Reed<sup>3</sup> it was found that pyridine, although not sufficiently toxic at a concentration of 1,000 parts per million to kill the wheat plants in nine days, was, nevertheless, very injurious, especially to the growth of the green parts of the plants. In a concentration as low as 50 parts per million the growth of the tops was inhibited and the leaf tips turned brown. In the lower concentrations there was no stimulation of growth.

Picoline ( $C_5H_4N.CH_3$ ), or methyl pyridine, was toxic to wheat seedlings, but only killed in the concentrations of 1,000 parts per million, and did not cause injury below 500 parts per million. The injury seemed to be manifested by the tops more than the roots, thus resembling the action of pyridine.

Piperidine ( $C_5H_{11}N$ ), or hexahydropyridine, killed and injured at a lower concentration than either pyridine or picoline. A sample of piperidine that was neutralized with acetic acid proved to be more toxic than the strongly alkaline piperidine itself. Piperidine seems to injure the roots more severely than the tops.

While picoline carboxylic acid may not be an important factor in the infertility of the soil studied, the fact that it has been found in other soils in larger quantities, its moderate toxicity, at least so far as wheat seedlings are concerned (although it is not impossible that toward other plants the compound may be either more toxic or less so) and its close relationship to other pyridine compounds of greater toxicity places it among organic soil toxins to be considered and sought for in the general study of unproductive soils.

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## A CHEMICAL EXAMINATION AND CALORIMETRIC TEST OF INDIANA PEATS.

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The lake region of northern Indiana, which is embraced in the three or four northern tiers of counties, contains hundreds of thousands of acres of peat bog. Twenty-nine representative samples of peat from this territory, obtained through the Department of Geology and Natural Resources of

<sup>1</sup> *Ann. Soc. Belge. Micr.*, 14, 29 (1890).

<sup>2</sup> *Czapek, Biochemie der Pflanzen*, II, 926.

<sup>3</sup> *Bot. Gazz.*, 45, 73 (1908).

Indiana,<sup>1</sup> were tested as to relative fuel value. Five specimens, typical of the varieties of peat found in Indiana, were subjected to a more complete chemical analysis, including the determination of moisture, volatile combustible matter, coke, fixed carbon, ash, sulphur, nitrogen, phosphate, potash and water absorbing power.

#### Methods of Analysis.

*Preparation of the Sample.*—The material was air-dried by spreading out in thin layers and exposing for about a fortnight to room temperature (20–25°). The air-dried peat was ground in a Weatherhead steel mortar to such fineness that all would pass through a 100-mesh sieve.

*Moisture.*—Five grams of the powdered, air-dried sample, contained in a weighing bottle equipped with a good fitting, ground stopper, were placed in a toluene bath which was kept at a temperature of 105°.<sup>2</sup> At the end of 48 hours the bottle was removed from the oven, stoppered, placed in a desiccator over fused calcium chloride for 30 minutes and then weighed. The drying for periods of 3–4 hours, cooling and weighing was repeated until the weight became constant. The operation usually required 72 to 90 hours.

*Calorimetric Test.*—The fuel value test was executed with 0.5 to 0.7 gram of oven-dried peat (105° C.) in a Parr calorimeter,<sup>3</sup> equipped for electrical ignition. The combustion of this quantity of peat in the presence of 1.0 gram of the chlorate mixture and one measure of sodium peroxide was complete.

*Notes.*—The finely powdered, oven-dried peat is exceedingly hygroscopic. The portion for this test should be weighed by difference from a stoppered tube directly into the combustion bomb. The charge of peat must not exceed 0.8 gram on account of the violence of the reaction.

The material dried to constant weight at 105° gives a somewhat higher thermal effect than would be obtainable in practice with air-dried peat, because of the moisture held by peat even after prolonged drying under favorable conditions. Fuels containing more than 2.5 per cent. of moisture must be dried at 105–110° before making the test in a Parr instrument. The further advantage in using oven-dried peat in these tests is that all samples may be accurately compared as to heating effect.

<sup>1</sup> Through the kindness of Hon. W. S. Blatchley, State Geologist of Indiana.

<sup>2</sup> 105° C. is recommended by Parmelee and McCourt in a report on New Jersey peats. *Ann. Report of State Geologist of N. J.*, 1905; 160° F. is recommended by Allen. (Davis on Peat, *Michigan Survey*, 1906.)

<sup>3</sup> THIS JOURNAL, 22, 646. A correction factor, made up from the heat of the wire and chlorate mixture, was used in the calculations of the heats of combustion of the peats. A factor incorporating correction for ash, combined water, sulphur, etc., as suggested by Parr (THIS JOURNAL, 30, 1606) would give a somewhat lower B. T. U.

*Evaporative Effect.*—The evaporative effect was calculated by dividing the heating effect in calories by 536.

*Sulphur.*—The sulphur was determined in the bomb residue from the calorimetric test by the volumetric method of Pennock and Morton.<sup>1</sup>

*Volatile Combustible Matter, Fixed Carbon, Coke and Ash.*—The determinations were made by the official methods recommended by the Committee on Coal Analysis to the American Chemical Society.<sup>2</sup>

*Note.*—The lid of the platinum crucible used in the determination of the volatile combustible matter must fit properly. A loose-fitting lid permits of appreciable loss of the light and finely divided material when the full flame is applied. This mechanical loss is greater with imperfectly dried material.

*Partial Analysis of the Ash.*—The ash for this purpose was obtained by incinerating 40–50 grams of peat in a platinum dish, at a low temperature, over a free flame.

*Potassium.*—1.0 gram of ash was treated according to the J. Lawrence Smith method.<sup>3</sup>

*Phosphoric Acid.*—0.5 to 1.0 gram of ash was treated with 25 cc. of hydrochloric acid and digested on the hot plate. After expulsion of the excess of hydrochloric acid, 2 cc. of nitric acid were added, the mixture boiled, filtered and washed. The phosphoric acid in the filtrate was determined by the method of Handy.<sup>4</sup>

*Nitrogen.*—The total nitrogen was determined in a 3.0 gram sample of air-dried peat by the method of Kjeldahl slightly modified. The peat was digested with 25 cc. of pure sulphuric acid, 10 grams potassium bisulphate and 1.0 gram copper sulphate (added after the first violent action subsided). The oxidation was complete in one to one and a quarter hours. The final distillation of the ammonia was accomplished with steam.

*Absorption of Water.*—The power to absorb water was determined for the purpose of demonstrating the efficiency of the air-dried, fibrous peats as a stock litter. An approximate determination was made, as follows: 5.0 grams of the coarse, air-dried, peat were covered with distilled water and stirred frequently during 12 hours. A folded filter paper supported in a funnel was filled with water and allowed to drain for 5 minutes. The moist paper was then removed to a small plain beaker and weighed (to second decimal) under watch-glass cover. The paper was again placed in position in the funnel, the peat collected upon it and, after 10 minutes' drainage, was removed to the beaker and weighed. The results are expressed as pounds of water absorbed by one pound of air-dried peat.

<sup>1</sup> THIS JOURNAL, 25, 1265.

<sup>2</sup> *Ibid.*, 21, 1116.

<sup>3</sup> *Fresenius*, Vol. II, 1175.

<sup>4</sup> Blair, *Chem. Anal. of Iron*, Sixth Ed., p. 104.

## Description of Samples.

No. 1. A sphagnum moss peat, well decomposed and dark chocolate brown in color.

No. 2. A mixed variety of peat from moss, grass, sedge, weeds and trees. Fibrous, fairly well decomposed and of light chocolate color.

No. 3. A grass and sedge peat, well decomposed and very dark brown in color.

No. 4. A sphagnum moss and sedge peat. Fibrous, imperfectly decomposed and light chocolate in color.

No. 5. A sphagnum moss peat. Finely fibrous, soft, incompletely disintegrated and dark brown in color.

No. 6. A moss, grass and sedge peat. Finely fibrous and light brown in color.

No. 21. A peat derived chiefly from sphagnum moss, well decomposed and dark brown in color.

No. 22. A moss peat, slightly fibrous, fairly well decomposed and chocolate in color.

## RESULTS OF THE ANALYSES.

No. of sample.	Air-dry.							Dry at 105°.		
	Percent. mois- ture.	Percent. vola- tile matter.	Per cent. fixed carbon.	Per cent. coke.	Per cent. ash.	Percent. nitro- gen.	Per cent. sul- phur.	Calories.	British ther- mal units.	Evaporative effect.
1	8.99	61.98	19.08	29.09	10.01	3.91	0.83	5525.6	9946.1	10.3
2	12.24	57.97	23.45	29.78	6.33	2.22	0.87	5466.8	9840.3	10.1
3	11.40	54.12	20.65	34.47	13.82	3.31	1.33	5013.4	9024.1	9.3
4	17.16	56.15	22.53	26.67	4.14	2.56	0.74	5684.8	10232.7	10.6
21	10.20	52.23	24.30	37.55	13.25	2.96	0.96	5503.1	9905.7	10.2
	No. of sample.	Absorption of water (air-dry).			Per cent. K <sub>2</sub> O in the ash.		Per cent. P <sub>2</sub> O <sub>5</sub> in the ash.			
	1	4.84			1.53		1.26			
	2	7.23			1.35		1.51			
	3	4.18			0.96		1.17			
	4	7.25			1.56		1.90			
	21	2.15			0.82		0.96			
	5	8.28			..		..			
	6	7.25			..		..			
	22	6.12			..		..			

The maximum heating effect found in the 29 samples tested, 10466.4 B. T. U., was given by a specimen of sphagnum moss peat from a bed 20 feet in thickness exhibiting almost perfect decomposition and very dark chocolate color. The minimum fuel value found, 4541.6 B. T. U., was given by an impure, highly oxidized peat, or muck, derived from grass and sedge. This sample, when dry, presented the appearance of brownish black soil. Excluding two samples of impure peat or muck which are

without commercial fuel value, the average heating effect given by the 27 samples of peat dried at 105° is 8957 B. T. U. The moss peats have a higher fuel value than the grass and sedge variety.

To afford a more exact comparison of the samples, and to determine whether or not the fuel value might be calculated from the proximate analysis, the volatile combustible matter, fixed carbon and ash have been calculated to the oven-dry (105°) basis, as shown in the following table:

	Volatile and combustible.	Fixed carbon.	Total volatile and combustible.	Ash.	B. T. U.
1	68.05	20.94	88.99	10.99	9946.19
2	66.02	26.70	92.72	7.21	9840.28
3	61.04	23.29	84.33	15.58	9024.15
4	67.77	27.19	94.96	4.99	10232.77
21	58.13	27.04	85.17	14.74	9905.70

In general, the higher calorific values have been obtained from the peats lowest in ash, and *vice versa*. However, this relation cannot be relied upon when the quantity of ash is within the accepted limits for high grade, commercially valuable peats, *e. g.*, peat No. 1 with an ash content of 10.99 per cent. gave higher B. T. U. than peat No. 2 with 7.21 per cent. ash.

The lack of regularity or relationship between the heating effect and the percentage of fixed carbon, or volatile combustible matter, is also worthy of note. An effort was made to modify the formula of Goutal,<sup>1</sup> for calculating the heating value from the proximate analysis of coal, by using an adjustable coefficient (A) for the volatile combustible matter, whereby the calorific power of peat might be approximated from the percentages of fixed carbon and volatile combustible matter. If the factor (A) be placed at 12,000 for 68 per cent. volatile combustible matter, and be increased or decreased by 250 for each per cent. of volatile combustible matter, a fair approximation of the calorimetric test is had in Nos. 1, 2 and 4;<sup>2</sup> the calculated values for 3 and 5 show wide differences. The application of an empirical formula for calculating the calorific power of peat is not possible because of the very great variation in the percentage of combustible in the volatile matter. There seems to be no close or definite relation between the thermal effect and any one of the factors determined in the proximate analysis of peat.

The analyses indicate that the best Indiana peat has a calorific value equal to the best grades of peat found in other parts of this country and in Europe.

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<sup>1</sup> *Rev. chim. ind.*, 7, 65. Goutal formula:

$$\text{Calorific Power} = \frac{8150 C + A \times \text{vol. comb. mat.}}{100}$$

<sup>2</sup> Error  $\pm$  about 60-65 B. T. U.