

their present laws, adopt the plan of reporting all of the available potash as shown by some modified method, and in so doing hasten the time when other states would change their laws.

The laws of the other twenty-seven states mentioned by the 1905 referee are probably modeled, as Mr. Booker has said, after the Massachusetts law "which was framed back in 1873 before we had experiment stations, when the idea was that only water-soluble materials were available."

LABORATORIES,
SWIFT FERTILIZER WORKS,
ATLANTA, GA., AND WILMINGTON, N. C.

ADDRESSES.

COAL ANALYSIS¹

By N. W. LORD.

Within the last few years the subject of coal analysis has become of great importance to many lines of industry. The demand for the analysis of coal has come from a great variety of sources and largely from those having little acquaintance with chemical methods and the interpretation of chemical results. The chemists, on the other hand, have been compelled to take such methods as were found at hand, and the result of these conditions has been not altogether satisfactory in many ways.

If we consider somewhat in detail the various determinations made in the laboratory in connection with coal testing, it will be easy to show how much is commercial and how little what might be called scientific. The so-called analysis of a coal is usually a practical test of purity of the material on a small scale, but it also involves determinations which are supposed in some way to indicate the nature of the coal itself.

To illustrate, suppose we consider an ordinary sample of bituminous coal. It may be assumed to consist, first, of an organic constituent composed of vegetable residues more or less altered but retaining traces of its original woody structure and composite character and containing as an integral part certain inorganic components. Like its source, woody fiber, it absorbs moisture in damp weather and gives it up in dry weather. The ultimate chemical composition of this material varies with the extent of the alteration, as shown in the peats, lignites and bituminous and anthracite coals, and also, in all probability, with the nature of the vegetation from which it has been derived. This extremely complex and indefinite material may be called "coal substance" for want of a better term. Intimately mixed with this are inorganic substances, probably mechanically introduced with the original vegetable debris or else precipitated by secondary reactions from circulating waters. These may be in the nature of clays or fine sand and also intimately mixed iron pyrites. I have examined samples of coal under the microscope, in which microscopic crystals of pyrites were scattered through the mass in sufficient amount to give high percentages of sulphur in the total,

yet in which a superficial examination of the coal itself practically showed no pyrites to the unaided eye. Other minerals may be present in the same way, even such unusual constituents as zinc blend, and, as Dr. Hillebrand has shown, considerable percentages of vanadium sulphide. The extremely complex nature of the organic constituents themselves may be inferred from the variable but sometimes very large amounts of sulphur they contain, well shown in the case of certain peats.

Now in addition to this base constituting the principal part of the sample submitted to the chemists for analysis, it has secondly, more or less coarse admixture of slate, clays and other rock-like material occurring in connection with the deposits of coal and not properly separated in mining, bone coal, and also streaks of cannel and other associated materials, coal-like in character, but differing notably even in the organic material they contain from the coal itself. The fact that many of these ingredients on standing or exposure to air rapidly alter by absorption of oxygen, evaporation, etc., makes it appear that the problem is still further complicated.

Now some of the things that the users of coal wish to know and for which they turn to the chemical analysis in the hope of receiving information are the following: the heating power of the coal; the amount of ash or inorganic matter left on burning the coal; the nature of the combustion of the coal, whether flaming, smoking, rapid, or slow; the gas-producing quality of the coal both as to yield and as to the nature of the gas; the nature of the ash yielded by the coal, whether fusible or not; the amount of sulphur the coal contains; the coking quality of the coal and the purity of the coke produced; and the possibilities of improving its quality by coal washing.

In addition to the above are many questions of special character, such as the nature of the coal substance, the relation of its composition to the previous geological history of the deposit, and the relation of total heating power to the heating power actually available for technical operations.

What are the analytical methods at present used in the laboratory to meet this series of questions and to handle this very complex material? Most of the laboratory work is done upon a sample which represents or is intended to represent the average composition of the material and which in no way recognizes the separate constituents of the very complex mineral aggregate of which it purports to be an average. The methods therefore give results only approximately related to the coal substance and difficult of general application.

We have as of generally recognized importance the ultimate analysis as ordinarily made, giving the determination of the hydrogen, the carbon, the nitrogen and the sulphur and the percentage of ash left after burning. This analysis also includes an estimate of the oxygen by difference, which is of course only approximate, and has been frequently pointed out in discussions of the subject. This ultimate analysis is capable of a high degree of accuracy for certain elements, which I think could be safely stated as within 0.05 per cent. in the case of hydrogen and perhaps 0.3 per cent. on carbon, 0.03 per cent. on the nitrogen and 0.05 on the sulphur. I do not mean that closer results are not obtainable, but ordinary work in the laboratory by competent chemists would, I think, run within

¹ Read at the Illinois Fuel Conference, Urbana, Ill., March 13, 1909.

these limits. The value of the ultimate analysis in all technical applications of the coal consists in its giving a reasonably accurate basis for the calculation of products of combustion and for comparisons with the heating power of the coal otherwise determined. The weakest point in the ultimate analysis is the uncertainty of its connections with the actual composition of the organic material as distinct from the impurities. Carbon, hydrogen and sulphur are present occasionally as carbonates, as combined water and as sulphates, respectively, in the slates and other mechanical admixtures, and the ultimate analysis does not distinguish between such occurrence and that in the coal substance. Ingenious efforts to eliminate these uncertainties as affecting the heating power by examination of various samples of the same coal differing widely in percentage of mechanical impurities have been made by several chemists.

In addition to the ultimate analysis, we have the more commonly made "proximate analysis," consisting of the determination of the moisture, ash, fixed carbon and volatile combustible matter in the coal. Much has been written in regard to these determinations.

On the same sample of coal closely agreeing results can be obtained on the ash and fairly close on the moisture. The variations in the volatile combustible is much larger and can only be kept within reasonable limits by very careful adherence to a defined method of procedure. The term moisture simply means the loss in weight under fixed conditions of treatment. It is intended and does bring the material to a condition which can be duplicated closely and represents a fixed basis for comparison, but in no wise stands for all the water in the coal. The volatile combustible, as has been carefully investigated by Professor Parr, is by no means properly named. Only a fraction, and a variable fraction at that, depending largely on the kind of coal, is combustible, and a considerable fraction, consisting of water vapor, carbon dioxide, nitrogen and other diluents is inert or non-combustible. It is well to recollect that the proximate analysis of coal was devised many years ago, and primarily as a means of testing the amount of coke left by coal. The volatile combustible has since been the subject of much discussion and many attempts have been made to correlate it with heating value, geological changes and the various questions arising in coal utilization. Some undoubted connections have been shown, but I feel that possibly too little recognition has been given to the empirical and more or less uncertain nature of the determination.

Of growing importance, particularly in connection with coal washing, and as a means for the study of coal samples, is the application of the separation by gravity or the so-called "float and sink" tests, in which the coal crushed to a moderate degree of fineness is separated on solutions of high specific gravity, chloride of calcium for specific gravities up to 1.35 and chloride of sulphate of zinc for higher specific gravities. Chloride of zinc solution can be made of a specific gravity as high as 2 and by dilution any of the intermediate gravities can be obtained. I have used this method in my laboratory for years to separate heavy mineral materials like slate and pyrites, as preliminary to the study of the composition of coal. The method is excellently adapted to tracing out the variations in composition as the intermixed mineral substances are eliminated. It will enable the experimenter to distinguish with considerable accuracy

between the inherent intimately mixed ash and sulphur compounds and the coarser and mechanical contaminations.

In recent years the leading factor in the commercial valuation of coals has become the calorific value or heating power of the coal and to-day the most important demand on the laboratory is the determination of this. The widely extending use of the bomb calorimeter is leading to new problems for the investigation of the chemists. Here again the heating value of the sample is modified more than by mere dilution by the nature of the mineral aggregate. As Mr. Turner and others have shown, the heating value is not entirely proportional in a given kind of coal to the residue left after deducting the ash and the moisture, but that there are factors depending on the influence of the inorganic material. Work of this kind is of great importance in order that the effect of ash, moisture and pyrites on the commercial value of coals may be more accurately known.

Calorimetry demands considerable training and experimental skill and the recently adopted policy of the Bureau of Standards of furnishing materials of known heating value so that the constants and correction of the calorimeter can be determined is greatly to be commended. The possibility of error in calorimetric determinations due to alteration of samples should be borne in mind. A very finely pulverized coal sample will oxidize in many cases very rapidly, and comparative results by different chemists on such a sample are liable to be very unsatisfactory unless all made at approximately the same time on samples that have been sealed in air-tight receptacles. Experiments made by the Fuel Testing Plant afford ample evidence of the extent to which this alteration may take place.

The determination of the water equivalent of the calorimeter experimentally gives rise to many difficulties and hence, except for those having had a great deal of experience in fundamental measurements, it is far better to use the calorimeter as a comparative instrument and depend for its constants upon burning substances of known calorific value such as are furnished by the Bureau of Standards. Commercial chemicals are quite variable and different samples of naphthalene, benzoic acid, etc., from different dealers will differ notably in their heating value. Recently the writer has obtained very successful results by the method of mixtures, adding hot water to the calorimeter from the Dewar flask or thermos bottle in which it is possible to read with great accuracy the temperature of the added water and to add the water to the calorimeter with only a very small correction for radiation loss during the addition. The method has proved successful in the hands of students who have made a number of water equivalent determinations agreeing within a very small limit of error with the calibration of the calorimeter obtained in other ways. Of course, this method has the advantage of being absolute and not relative.

The foregoing outline has dealt with the laboratory side of the question. All the analytical work, calorimetric work and everything else in connection with the testing depends for its economic value on the fundamentally representative nature of the sample of coal tested in the laboratory. Here is the weakest point in the commercial application of the results. Coal sampling is a matter now prominent before the technical world. Now that the extending

recognition of the value of laboratory work is leading to the purchase of coal on chemical specifications the whole question of sampling is under review. Ingredients most affected by sampling are obviously moisture, ash, sulphur, and calorific value. In a recent paper of great interest Mr. E. G. Bailey has presented a large number of results in which he criticizes existing methods and lays down certain general deductions from carefully conducted experiments as to the general principles involved in the securing of correct samples. Mr. Bailey has, in my opinion, done a very valuable piece of work both in calling attention to the importance of the subject and in the experiments that he has brought forward. As having been connected with the government work at St. Louis, I feel called upon to correct certain misapprehensions in regard to that work which I think have unintentionally on his part led him to place in a somewhat false light as to the accuracy with which the sampling was done. As I follow his paper he makes a fundamental assumption that the variations in the portions of coal taken at the plant from the same car shipment and sent to the Boiler, the Gas Producer and Briquetting and Washing Plants were identical in composition with the car load samples and that the variations shown in these different portions were due to variations in sampling of the portions at the various plants, whereas, the facts of the case are that the different portions taken from the car were not supposed to be sampled from the car but simply portions unloaded at different points, and the reason why analyses were made of the separate portions was because it was recognized that the car load was not uniform as far as contents of ash, sulphur, etc., were concerned, and that the car load analysis could not be taken for the different portions without a preliminary thorough mixing of the whole car load, which was not practical. This is clearly stated on page 284 of Professional Paper 48, Part 1, from which I quote:

It was intended that the car sample should represent the average of the whole car, while the other samples stood for different portions of it. These would average about 5 tons each. In some cases the car sample was taken on only a part of a car. The large variation in the different samples in a few cases shows the irregularity in the coal in the car.

Experiments were made at St. Louis and published in this same work, giving the analysis of duplicate samples, and while the results were not very satisfactory and some errors were found, they were not of the magnitude given by Mr. Bailey from his comparison of the other samples based on the assumption which I have shown was not warranted and which was contrary to the facts as we stated them at the time. Br. Burrows has discussed the question of mine samples, but the comparison of these with coal shipped from the mines makes no allowance for the extent of cleaning that the coal underwent in shipping and in taking the mine samples. As stated, several duplicate samples on the car loads were run to check the St. Louis sampling and the worst result obtained, I think, was the one given on page 287, in which an extreme variation in ash on a coal averaging 15 per cent. ash was a little over 2 per cent. This coal was selected as the worst obtainable from the standpoint of sampling and the variation of the highest and lowest samples from the average of all the experimental samples on this coal was only a little over one per cent. Notwithstanding this criticism that I felt compelled to make of Mr. Bailey's representation of the St. Louis work, I feel that this general

proposition in regard to the uncertain nature of much coal sampling is well sustained. His conclusion as to the amount of sample necessary in order to obtain a representative sample are of great interest. However, I do not feel that the difficulties are quite as great as his experiments would lead one to conclude.

Two things are important to consider:

In the first place, that in crushing coal a large proportion of fine material is produced so that the average size of particle is but little more than one-half the maximum size and therefore results on the distribution of the maximum size pieces greatly aggregate the difficulties. I recently took four samples of screened coal and had them put through a jaw crusher and screened.

In No. 1, 8.8 per cent. was retained by a $1/2$ " screen and 56.4 per cent. passed a $1/4$ " screen. This sample of coal was sampled in duplicate at this state of crushing, portions of coal of about five pounds being taken. The two five-pound portions were each separately pulverized, well mixed and analyzed. The first portion gave 13.86 per cent. ash and the second portion 13.56 per cent. A similar experiment on a second sample of coal gave 16.3 over a $1/2$ inch screen and 46.65 per cent. through a $1/4$ inch screen. The ash in the first sample, 14.59; in the second sample, 14.49. A third sample of coal gave 7.3 per cent. over a $1/2$ inch screen and 48.3 per cent. through a $1/4$ inch screen. The ash in the first sample was 15.11; in the second sample, 15.10. In two of these samples the percentage of ash in the finer portion was considerably greater than the percentage of ash in the coarser portion.

Of course, these results are too few in number to amount to anything, but they show that the finer material is in sufficient proportion to diminish the irregularity introduced by the bad distribution of the coarser lumps in the sample.

A further point in coal sampling which has to be considered is that in the larger sizes there is a natural mixture in the material of the slate and the coal, so that 4-inch lump coal does not represent a mixture of 4-inch lumps of coal and 4-inch lumps of slate to any appreciable percentage of the ash present. In other words, the inspection element must enter coal sampling, and no man would draw a moderate sized sample of a coal in which he has a large percentage of lumps of slate as large as the lumps of coal, while the occasional presence of even a large lump of slate would have but little influence on the ash percentage of the resulting sample.

Mr. Bailey gives what he names the size weight ratio or the relation between the maximum sized piece of coal in the sample and the weight of coal necessary to take in order that the sample may be certainly representative within an error of one per cent. of ash.

Now his figures lead to very large samples in cases of lump coal, but the foregoing indicates that the size ratio should probably be that of the maximum slate sizes present in the coal lumps, or free, rather than the actual coal lump size. The moderate variations in the ash percentage of the different lumps would have far less influence in disturbing sampling than the presence of equivalent sized lumps of slate.

Obviously, therefore, careful inspection must precede the sampling in the case of lump coal and the presence of large pieces of slate and pyrites in lumps in the coal taken into

consideration in determining the size of sample necessary in order to properly sample the coal.

I have always directed samplers to inspect the coal carefully and break up into small pieces any lumps of slate, bone coal or pyrites found or anything else that did not look like coal before taking or dividing the sample.

Of course, it is well known that no system of sampling which is purely mechanical is satisfactory for materials in which coarse distribution of the components exists, unless the whole of the material is crushed to approximately such limits as are defined by Mr. Bailey. This is the principle involved in the sampling of lead and copper, and gold and silver ores, where the system of sampling involves the crushing of many tons of material. Such a system of sampling is, of course, out of the question with lump coals where the crushed material would be to a certain extent rendered of small value. The system of sampling adopted in this case must be based upon an estimate of the maximum size of slate and pyrites, constituting an important portion of the impurities.

The difficulty of eliminating the personal element in doing such sampling is one of the problems which the Committee on Specifications will have to contend with. Meanwhile, the sampling problem is before us and must be adequately solved before the laboratory analysis of the coal reaches its full application.

The preparation of the laboratory sample from the field sample is a much more simple matter and is easily within the reach of present methods. One of the principal difficulties involved at this point is the avoiding of changes in the composition of the sample due to loss of moisture and to oxidation. I notice in many experiments the coal is ground to 100-mesh or even 200 before analysis. I think this is a step in the wrong direction. The finer the powder the more prone to oxidation and loss of moisture, and I think the effort of the sampler should be to determine a lower limit for Mr. Bailey's "size-weight-ratio" as well as a higher, and not to reduce the sample beyond this point, before weighing out for analysis.

We have considered that a sixty-mesh sample will meet the ordinary requirements where 1 gram is taken for the determination, which is within Mr. Bailey's figures as I understand them.

REVIEW.

PHARMACEUTICAL CHEMISTRY DURING 1908.

(Concluded from page 260.)

Organo-Therapeutics or Organo Remedials.

The first to call attention to this class of remedials was Brown Séquard, who advanced the hypothesis that "all glands of the body give to the blood useful principles, the absence of which is felt when these glands are extirpated or destroyed by disease." This hypothesis was extended to include various organs and that in a diseased condition of an organ, an extract prepared from the same organ of a healthy animal serves as a remedial agent. The efficacy of extracts of certain organs may be best judged by the success attending the use of such preparations as Iodothyryn (thyroid ext.), suprarenal preparations, testaden, spermin

(testacle ext.), ovaraden (ovaries ext.), manimae (udder ext.), Linadin (spleen ext.), etc. New in this line are:

Manimin, an extract of the mammary glands, useful as hemostatic in uterine hemorrhage.

Paratoxin, a toxin obtained from bile and used in tuberculosis.

Leciferrin, a lecithin iron preparation from egg yolk.

Neuroprin, an extract of the nerve tissues useful in nervous diseases and as an antidote in strychnine poisoning.

Pancrobilin, a nucleo enzyme from the pancreas and gall, useful in constipation.

Orchicithin, an extract of the testes of the ox which is employed in sexual neurasthenia.

Astauxin, a calcium paranucleinate used as antirachitic.

Cellasin, a carbohydrate and fat splitting-ferment claimed to hydrolyze 3000 times its weight of starch or sugar.

Alkaloids and Glucosides.

Among the purin derivatives, Theophyllin (Theocin), a 1.3-dimethyl, 2.6-dioxypurin and its alkali double salts, still maintains a front rank among the diuretics. Through interaction between theobromin and monochlorhydrin, a dioxypopyl-theobromin has been prepared (Bayer, D. R. P. 191106). In an analogous manner, a 1.3-dimethyl-7-oxyethylxanthin has been prepared from theophyllin and glycolhydrin. Paraxan, a dimethylamino derivative of 1.7-dimethylxanthin, introduced by Boehringer and Sohn, has been withdrawn because of its irritant gastric action. Schwabe¹ has prepared various alkyl derivatives (ethyl, propyl, benzyl) of theophyllin and through oxidation of ethyl theophyllin, he obtained a dimethylparabehenic acid. These products are still in the experimental stage. A new diuretic is the double salt of theobromin sodium and sodium lactate called Theolactin.²

Morphine Derivatives.

The hydroxyl groups present in morphine are intimately associated with its toxic action, which, through its narcotic characters, differs from all other opium alkaloids, its action being chiefly upon the nerve centers of the brain. Upon closing these OH groups by substituting one or both of these hydrogens by alkyl or acetyl radicals, the narcotic characters disappear, while on the other hand, a spinal excitant (tetanic action) is developed. Thus, codeine produces, like morphine (but in lesser degree) narcosis, followed by an elevated reflex, which, if the dose be sufficiently large, develops tetanic convulsions. This action upon the spinal cord increases with the number and molecular weight of the alkyl groups introduced; hence codethylene, with its ethyl group, is more intense in action than codeine, which contains but one methyl group. Among all possible derivatives, it is immaterial as to whether an acetyl or alkyl radical, aliphatic or aromatic, is introduced. There is practically no qualitative difference in action so long as the same hydrogen is replaced. During recent years a number of derivatives of the codeine type have been introduced. These substances, while less active for relieving pain, exert a sedative effect on the unstriated muscles of the bronchi, and reduce the disposition to cough; hence are of value in phthisis, bronchitis, asthma, etc. Among these were Dionine, the hydrochlorid of ethyl morphine ($\text{HO.C}_{17}\text{H}_{17}\text{NO.O.C}_2\text{H}_5$,

¹ Ber. d. chem. Ges., 40, 1744.

² Chem. Ztg., 1908, 367.