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A MODIFICATION OF BERTHIER'S METHOD FOR THE
ASSAY OF FUELS; AND ITS APPLICATION TO THE
TECHNICAL DETERMINATION OF THE HEATING
POWER OF BITUMINOUS COALS.

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Berthier's method as ordinarily employed consists of heating for about one hour, ultimately to the point of fusion, a mixture of the fuel with forty times its weight of litharge, using a like quantity of the latter to cover the mixture. The weight of the resulting lead button is then taken as a measure of the comparative heating power of the fuel.

This method, although frequently used, does not always furnish trustworthy results owing to a number of causes, the principal of which seems to be the reducing action of carbon monoxide which with other furnace gases is diffused through the more or less porous material of the crucible, and, in the case of bituminous coals the escape without decomposition of gaseous or highly volatile hydrocarbons.

But, notwithstanding these objections, it is the only simple and expeditious method that has been devised for determining the capacity of a fuel for oxygen, consequently whatever tends to promote its efficiency will be worthy of notice.

Years ago, in discussing the merits of Berthier's method, Mitchell proposed the substitution of lead-carbonate for litharge, the latter being always contaminated with minium while the former on heating without access of air is reduced to pure lead-oxide. But this modification merely removes a minor objection. In a series of

about 50 duplicate assays, in which lead-carbonate was substituted for litharge, the writer found the results to be extremely variable and untrustworthy. Operating with a small Fletcher gas-furnace and using 5-gram luted crucibles the yield of reduced lead from charcoal and anthracite, during 20 minutes heating, finally to fusion, usually exceeded by about one-fifth that required by calculation, calling to mind the results obtained by Dr. Ure in similar experiments. With bituminous coals the amount of reduced lead was generally but slightly in excess when the assay was heated for the same length of time, owing to the escape of undecomposed hydrocarbons; but even then the reduced lead would be largely in excess if the heating was prolonged an additional 10 minutes preceding the final fusion; a result which can only be attributed to the diffusion of reducing furnace-gases.
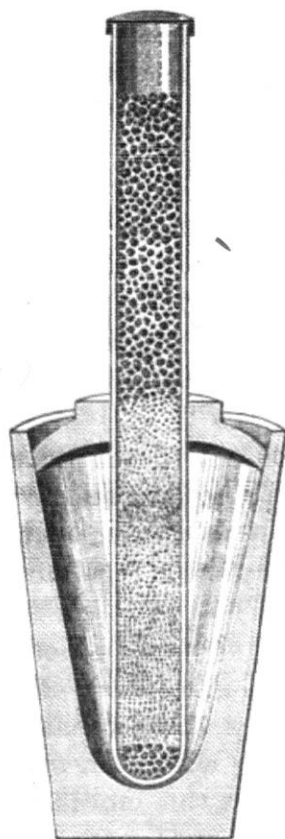
No doubt these discrepancies are excessive and much greater than would be experienced if the operations were performed in a muffle or specially constructed furnace with crucibles of fine texture; but they serve to illustrate how much the result depends on the density of the crucible and the absence of volatile hydrocarbons. A consideration of these objections led to the following modification which gives both in the muffle and gas-furnace very concordant results. 2 decigrams of the fuel, finely powdered and accurately weighed, is intimately mixed, by grinding in a porcelain mortar, with 10 grams of dry lead-carbonate.

This mixture is introduced into a short tube of combustion-glass, about 14^{cm} long, 15^{mm} interior diameter, and 1.5^{mm} thick, containing 3 decigrams of

Fig. 1.

borax-glass in the closed end. The mixture is then covered to a depth of 7^{cm} with grains or pellets of lead-carbonate such as will not pass through a 60-mesh sieve (24 meshes per centimeter) and a cap of thin sheet-iron adjusted loosely on the open end of the tube. Thus prepared the tube is placed in an upright position in a 5-gram clay crucible (7^{cm} interior height) to which is fitted a thin sheet-iron cover, turned down so as to grasp the rim of the crucible, and having a hole in the center a trifle larger than the tube, through which the latter projects about one-half its length.

Instead of an iron cover, one made out of a small scorifier rasped down so as to fit into the crucible, in the manner shown in the diagram, will be preferable. If the assay is conducted in a muffle the temperature at first should not exceed a very dark, or just visible, red-heat, to avoid fusing the lead-oxide in the exposed part of the tube, before the mixture, shielded from the heat by the crucible, has been decomposed, and for this reason it is best to place the assay well towards the door. The temperature is gradually raised until at the expiration of about 20 minutes the rear half of the muffle is at a full-red heat. The crucible is then transferred to this part of the muffle and the contents of the tube, which by this time has shrunk to two-thirds of the original volume, allowed to fuse for about 10 minutes, when the operation is finished and the fused mass, expanding the lower end of the tube to the form of the crucible bottom, becomes sealed and protected from oxidation by the doubling over of the exposed part of the tube.

About the same length of time is required if the assay is performed in a gas, or gasoline, furnace, observing in regard to temperature that it is only necessary, until the reduction of the lead-carbonate is effected in the upper half of the tube, to use a blast sufficiently strong to force the gas into the furnace, allowing it to ignite around the tube above the crucible. The blast may then be increased

so as to bring about decomposition of the contents of the lower half of the tube, care being taken to keep the temperature below the fusing point until the contraction of the assay indicates that decomposition is finished.

Throughout the operation the assay is protected from the reducing action of objectionable gases, while atmospheric oxidation is prevented by the constant evolution of carbon dioxide. The primary heating of the upper half of the tube, causing the rapid reduction of lead-carbonate to lead oxide, prevents the escape, without decomposition, of hydro-carbon gases and vapors.

The crucible is broken when cold, the lead button hammered free from slag, brushed clean and weighed. The maximum difference in the weight of lead obtained from separate assays of the same fuel will rarely exceed one-half of one per cent. and is usually within three-tenths.*

The following precautions should be observed in preparing and making the assay. If not convenient to prepare the lead-carbonate in a pure state the best commercial " flake-white " may be substituted. It should be tested for lead-sulphate, chloride and oxychloride, as well as zinc compounds, either of which, if present, would interfere with the accuracy of the results. It is also necessary to prove the absence of acetates. Other organic matter, such as dust particles, may be floated off by water. When dried the carbonate is separated into two portions by sifting, that which remains on the sieve being used to cover the assays. There must be sufficient lead-oxide in the carbonate used to effect the complete decomposition of the admixed fuel, otherwise when fusion takes place the lead-oxide in the upper part of the tube will come in contact with undecomposed particles of fuel and the violent evolution of carbon-dioxide may cause the assay to boil over. After filling

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* With bituminous coals the amount of contained oxygen that will combine either with carbon or hydrogen, as the case may be, will depend largely on the temperature employed and will slightly influence the yield of reduced lead: for which reason the results are not likely to correspond exactly unless the assays are conducted simultaneously at the same temperature and with the same sized crucibles.

the tube, form a passageway for escaping gases by tapping lightly while in a nearly horizontal position. Use combustion glass tubing if possible as it will retain an upright position until the lead-oxide is fused: nevertheless common glass tubing can be used if care is taken to support it until the fused mass disappears into the crucible. Unless borax glass is placed in the bottom of the tube the lead button will contain litharge and will not be malleable.

Accurate weighing is indispensable, as any error will be multiplied as many times as the weight of fuel is contained in the amount of reduced lead.

With regard to the practical utility of the foregoing method in estimating the value of a fuel much will depend on the purpose for which the fuel is used. For instance when it is necessary, as with blast furnace fuel, to determine the constituents of the ash, an ordinary proximate analysis will most conveniently give the desired information. But with bituminous coals and lignite used in the reverberatories of metallurgical works, or in large quantities by other industrial establishments, the character of the ash is of secondary importance. In this case by the method here suggested the comparative heating power is readily obtained and the result will compare favorably with the value deduced from an elementary analysis which will require several hours to perform and after all leave the operator without any knowledge of the condition in which the oxygen exists either in the coal or when liberated from it previous to combustion. Moreover industrial laboratories are not always provided with the requisites for organic work. The ordinary proximate analysis while giving much valuable information in regard to the character of the fuel, and also comparable results in the hands of any one operator, will yield variable results on the same fuel in the hands of different operators, so much being dependent on temperature, weight of fuel and size and kind of crucible employed. Even the results obtained by one person are not always trustworthy or to be relied

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on as a basis for comparison, for of two samples of bitu-
minous coal that yield about equal amounts of fixed carbon
and volatile substances the gaseous products of the one
may give a much higher percentage of carbon monoxide,
carbon dioxide, and aqueous vapor, than the other, and
therefore a lower calorific power.   The comparative value
of the vapors and gases will be indicated by the amount
of lead reduced by the coal.   The following analysis, made
under the same conditions, of coal from four widely
separated Colorado coal fields will illustrate this point:

	Canon City.	El Moro.	South Cañon.	Langford.
Moisture	5.1	0.7	5.4	15.7
Volatile Matter	36.6	33.5	38.2	34.1
Fixed carbon	54.2	53.4	53.3	47.
Ash	4.1	12.4	3.1	3.2
Parts of lead reduced by one part of fuel	26.12	27.34	26.77	23.40
Parts of lead reduced by fixed carbon	18.69	18.42	18.38	16.21
Parts of lead reduced by volatile matter	7.43	8.92	8.39	7.19

Regarding the value of El Moro coal gas as 100 that
of the others will be, South Cañon 92, Cañon City 83 and
Langford 80.

Cañon City coal is the standard for domestic uses in
Colorado, Kansas and Nebraska.   It is a non-caking coal,
the flame being remarkably free from soot.   The gas from
El Moro coal is well adapted for illumination and is used
for that purpose by the Denver Gas Company.   South
Cañon, on Grand River, furnishes a slightly-caking domes-
tic coal with a long flame, rather more sooty than that from
Cañon City coal.   Langford coal is the best quality of the
lignitic variety from Northern Colorado.   It would appear
therefore that something more than a mere proximate
analysis is necessary for the valuation of bituminous coals,
or to enable one to compare the results of different assay-
ists, and when it is not practicable to subject such fuels to

an ultimate analysis the method above described might be partly or wholly substituted.

When calculating the calorific power of a fuel from the results obtained by this method some account must be taken of the kind of fuel operated upon. In the case of charcoal, coke, and the better qualities of anthracite, it may be sufficient for practical purposes to assume, as is ordinarily done, that the reduced metal represents a certain number of carbon heat units, or, in other words, to compare its value with that of pure carbon; but in an assay of bituminous, semi-bituminous and sand coals, or lignite, it will be advisable to make a correction for hydrogen, otherwise the value, as compared with that calculated from an ultimate analysis, will be too low by from 100 to 400 heat units, according to the character of the coal. If the relative proportions of carbon and hydrogen in coal were always the same the amount of reduced lead would indicate very closely the comparative heating power; but the proportions of available hydrogen in different kinds of coal may vary as much as 3 per cent., or even more in extreme cases, so that the reduced lead simply indicates the capacity of the fuel for oxygen. Muck* states the average amount of disposable hydrogen in the different kinds of coal to be as follows: Lignite, 3 per cent.; gas coal, 4.5 per cent.; coking coal, 4.5 per cent.; semi-caking and sand coal, 3.5 per cent.; and anthracite, 1.5 per cent. While this statement may be accepted as generally true when applied to the Carboniferous coals of Europe and Eastern North America, an ultimate investigation of the different kinds of Cretaceous coals occurring in the Rocky Mountains may show that in their case the above figures do not hold good; Cañon City coal for instance contains, according to Potter and others, between 6 per cent. and 7 per cent. of disposable hydrogen. However, in most of the Rocky Mountain Cretaceous coals which have thus far been analyzed, the percentage of available hydrogen corresponds very closely with Muck's

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* Steinkohlen Chemie.

figures, which are generally applicable as representing approximately the disposable hydrogen in each kind of coal. Taking these figures as a basis, the correction for hydrogen depends on the following considerations: one part of lead reduced by carbon corresponds to $\frac{8080}{34.5} = 234$ carbon calories. One part of lead reduced by hydrogen corresponds to $\frac{34.462}{107} = 322$ hydrogen calories. 34.5 being the parts of lead reduced by one part of carbon corresponding to 8080 carbon calories, and 107 being the parts of lead reduced by one part of hydrogen corresponding to 34.462 hydrogen calories. But one unit of hydrogen reduces 1.07 of lead, consequently for each unit of disposable hydrogen present there are $88 \times 1.07 = 94$ heat units to add to the value found assuming that all the lead has been reduced by carbon.

To explain this matter more clearly take the case of coking coal from Coal Basin, Colorado, or from Elk Garden, West Virginia, which reduces about 31 times its weight of lead by this method. The equivalent in carbon calories is 7.260, which added to 423, the correction for 4.5 per cent. of disposable hydrogen, gives a total of 7.683 heat units. That is, there are 26.185 parts of lead, corresponding to 6.132 + heat units, reduced by carbon, and 4.815 parts of lead, corresponding to 1.550 + heat units, reduced by hydrogen. By making this correction the value obtained will approximate very closely that deduced from an ultimate analysis, which, however, it may be well to remember, is usually lower than that actually developed by the calorimeter, owing probably to the necessity of regarding all the oxygen present as combined with hydrogen, whereas a large part may be also in combination with carbon, or combine with carbon at the moment of evolution.