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NEW METHOD
OF
DETERMINING THE CARBON
IN
NATIVE AND ARTIFICIAL GRAPHITES, &c.

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It is well known that native graphite and the graphite of cast iron resist the usual oxydating agents with great obstinacy. Schafhaeutl, in his elaborate paper on "the different kinds of iron,"* states that "concentrated nitric acid dropped on the red hot graphite (of iron) has not the slightest action on it; neither has sulphuric acid dropped into boiling nitric acid." He found that "with the exception of hydro-fluoric acid, no single chemical liquid seemed to have any action on those scales, and only the most concentrated hydro-fluoric acid slowly attacked them when in a state of most minute division." Similar results have attended our trials with various specimens of native graphite. The method by which Schafhaeutl succeeded in effecting a complete

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* Phil. Magazine, vol. xvi.

oxydation, was by dropping nitric acid into hot sulphuric acid surrounding the graphite and then boiling the liquid until all the nitric acid was decomposed. But he adds, it was only after a repetition of the process for the fourth time, that the last trace of graphite had disappeared and the acid remained perfectly clear.

The method about to be described, compared with the preceding, is easy of execution, and if we may judge from our experiments, is capable of yielding uniform and accurate results. We trust, therefore, that it may be thought worthy of the attention of analytical chemists. *As a means of comparing the purity of the different varieties of native graphite*, we have found it entirely satisfactory. As applied to the still more important purpose of determining the entire amount of carbon in the several kinds of cast iron and steel, our experiments have not yet been sufficiently numerous to enable us to pronounce confidently upon its accuracy, but we are not without hopes of making it available also for this object, as a substitute for the very troublesome procedure by organic analysis.

The oxydizing agent employed in this process is a mixture of *bichromate of potassa and sulphuric acid*, which, when applied to the graphite, under the conditions about to be described, converts the carbon rapidly and completely into carbonic acid. The gas being intercepted by a Liebig tube, gives, by the equivalent of carbon, the amount of this substance present in the graphite. The details of the method are as follows:

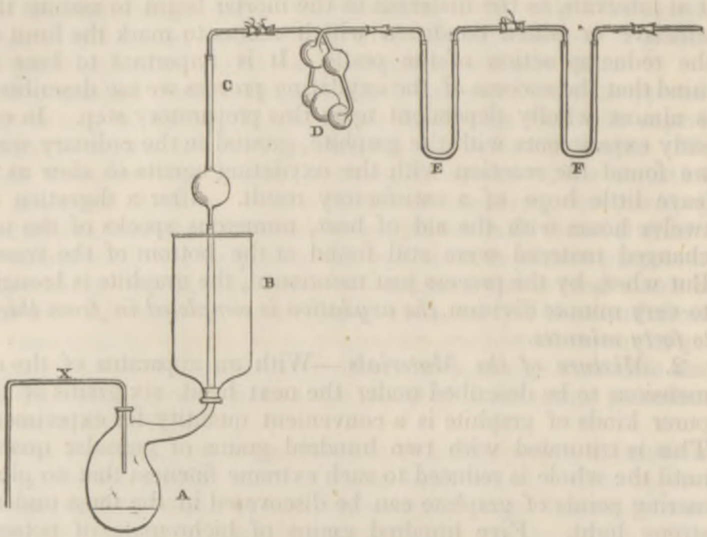
1. *Preliminary treatment of the Graphite.*—As the native graphite not unfrequently contains adhering organic matter and a trace of earthy carbonate, both of which would add to the carbonic acid evolved in the process, it is proper after reducing the mass to a coarse powder, to moisten it with dilute sulphuric acid, and expose it to a red heat for a few minutes. It must then be brought to a state of *extremely minute division*. This great comminution, which is indispensable to prompt and entire oxydation, can not be affected by grinding in the usual way, as the graphite thus treated, forms flakes or plates under the pestle. But the requisite subdivision is readily attained by grinding it in a Wedgewood mortar with pure quartzose sand, or what is better with small fragments of granular quartz. The material we use for this and other similar purposes, is a very pure white granular quartz, found in a thick vein in the neighborhood of the University. It readily yields under the pestle, and may be reduced in a few minutes to an almost impalpable powder. Pumice stone we have found equally efficient, though somewhat more difficult to break down. Any trace of the graphite that may adhere to the mortar, is completely washed out by trituration with a small additional portion of the siliceous matter.

To obtain the requisite subdivision we use a weight of the silica, from thirty to thirty-five times that of the graphite, adding it at intervals, as the materials in the mortar begin to assume the adhesive or caked condition which seems to mark the limit of the reducing action of the pestle. It is important to bear in mind that the success of the oxydating process we are describing, is almost wholly dependent upon this preparatory step. In our early experiments with the graphite, ground in the ordinary way, we found the reaction with the oxydating agents so slow as to leave little hope of a satisfactory result. After a digestion of twelve hours with the aid of heat, numerous specks of the unchanged material were still found at the bottom of the vessel. But when, by the process just mentioned, the graphite is brought to very minute division, *the oxydation is completed in from thirty to forty minutes.*

2. *Mixture of the Materials.*—With an apparatus of the dimensions to be described under the next head, six grains of the purer kinds of graphite is a convenient quantity for experiment. This is triturated with two hundred grains of granular quartz, until the whole is reduced to such extreme fineness that no glimmering points of graphite can be discovered in the mass under a strong light. Five hundred grains of bichromate of potassa, previously powdered, must now be mixed intimately with the silica and graphite by grinding in the mortar. Introducing the mixed powder into the retort we add one cubic inch of water, and after suffering the liquid thoroughly to penetrate the mass, we pour upon it, slowly, five cubic inches of sulphuric acid of the ordinary density, using occasional agitation as we proceed. The reaction may be aided by a gentle lamp heat applied a few moments at a time; but it soon becomes as rapid as desirable, the carbonic acid passing into the absorption tube and the liquid acquiring a greenish color around the edges where the adhering particles of graphite are greedily consumed. During the process, the lamp heat is to be renewed, whenever necessary to maintain a steady moderate stream of gas, and in closing the operation, it should be applied for several minutes, to favor a copious evolution of oxygen, which, driving most of the carbonic acid before it, diminishes the necessity of a long continued aspiration at the end.

The *large excess* of bichromate of potash and sulphuric acid used in this process, is requisite to ensure a prompt and complete oxydation. Any further dilution with water retards the action. The sulphuric acid, in the proportion mentioned, is adequate, not only to secure an abundant development of chromic acid, but to maintain the mixture in a sufficiently fluid state to prevent any serious intumescence while the oxydation is going on.

3. *Apparatus used in the Process.*—This will be understood from the accompanying diagram and description.



A is a glass retort having a capacity of about thirty cubic inches, which we have found large enough for operating conveniently on six grains of pure graphite. Its beak is bent obliquely and then vertically upwards so as to present an erect stem for about twelve inches, which is enclosed by a glass jar B nearly filled with water. This is designed to condense any vapor of sulphuric acid, which may be evolved from the mixture at a high temperature, and which by passing into the adjoining chlorid of calcium would liberate hydrochloric acid and thereby increase the weight of the potash tubes. The drying tube C, about ten inches long, is charged in the straight part with dry chlorid of calcium and in the bulb with loosely packed cotton, and is joined to the beak of the retort by a cork and cement. D is a common Liebig tube, containing the standard solution of potassa, and E is a small U tube charged with fragments of potassa, having at each end a little flock of cotton. The latter serves to intercept any carbonic acid which might escape absorption in the Liebig tube. The amount thus passing which is extremely small, is entirely arrested before reaching the second U tube, F. This is added to prevent the reflux of CO_2 or aqueous vapor into the preceding tubes, during the slight *recoiling* pulsation caused by the intermitting transit of the bubbles. The remote end of F communicates with a large aspirator, through the medium of a leaden tube and gallows screw, as so usefully and variously applied by Dr. Hare.

The connections from C to the aspirator are of gum elastic tube. D and E are united above by a thin wire with a hook, for convenience of suspension in weighing them together, before and after the operation. In the tubulure of the retort, passing through a tight cork, is a slender glass tube X, doubly bent and descending nearly midway. It is drawn out to a long taper and hermetically sealed at the far end. Its chief use is to admit a current of air during the aspiration, which forms the closing step of the experiment. But it is also useful as a means of introducing more sulphuric acid, should we find, late in the process, that enough has not been added to complete the oxydation of the graphite. This is done by removing the tip of the tube X with a file, and bringing a vessel containing sulphuric acid up around the open end. The aspiration gently draws the liquid into the retort, and now the opening of the tube may be stopped by a little ball of softened wax or cement. As however with the proportion of materials previously stated, such a recharging will scarcely ever be necessary, this appendage may be replaced by a vertical tube similarly sealed, to be opened only for the final aspiration.

4. *Mode of Manipulation.*—On this head little need be added to what has been included in the preceding details. A brisk but not too violent evolution of CO_2 is to be maintained, by applying or withdrawing the heat, and by occasional slight agitation. Soon after the last remnants of carbon have been consumed, the bubbles in their passage through the Liebig tube indicate by their persistent volume the completion of the oxydation. But as a further security we accelerate the evolution of oxygen by the lamp, and continue to maintain this stream of passing gas for several minutes.

We now remove the neb of the tube X, and by aspiration pass slowly through the apparatus a volume of air some two or three times the capacity of the retort and connections. The potash tubes may then be removed and weighed.

Where there is doubt as to the completeness of the oxydation, and indeed as a means of assurance generally, the contents of the retort should be transferred to a large porcelain dish by repeated washings. After copious dilution the insoluble matter quickly subsides, and the liquid can be almost entirely removed with a syphon. Should even a very minute quantity of the graphite remain unconsumed, it can be readily detected either with the naked eye or with a magnifier, in consequence of the strong contrast of its color with the whiteness of the siliceous powder. In this way we have found that an amount of the divided graphite can be discerned, so small that, estimating it as carbonic acid in the absorption tubes, it would not affect sensibly a good balance. At the commencement of the experiment and before adding the sulphuric acid, the usual precautions are observed to ascertain the closeness of the junctures, by using the aspirator.

5. *Results of Analyses made by this Process.*—The details which follow include the analyses of three varieties of native graphite, differing in purity, two specimens of kish or the graphite of iron, and a specimen of a peculiar carbonaceous sublimate deposited during the combustion of native carburetted hydrogen gas.

Native Graphite, (*a.*)—The mineral here referred to is a beautiful crystalline variety, found associated with more massive impure graphite, in a very micaceous gneiss, in Albemarle county, Virginia. It consists of long flat narrow plates or prisms, arranged parallel to one another in close bundles of a curved form, presenting a structure somewhat resembling that of certain thin veins of asbestus. Between the plates are occasional thin partings of brown siliceous matter, but the body of each crystal appears to be perfectly pure graphite.

Six grains of this material reduced to an extremely fine powder with the granular quartz, yielded by oxydation, carbonic acid, 20·76 grains. A second experiment with a like quantity gave, carbonic acid, 20·82 grs.

From the near coincidence of these results, we may safely assume the mean 20·79 as a basis for computing the carbon in the mineral. We infer therefore that this graphite contains in 100 grs., carbon, 94·5 grs.

Native Graphite, (*b.*)—This is a compact massive variety, from Cumberland, seemingly very pure.

Six grains yielded, in two successive experiments—first experiment, carbonic acid, 20·35 grs.; second experiment, carbonic acid, 20·31 grs. Assuming the mean 20·33 for computation, we have in 100 grs. of this graphite, carbon, 92·4 grs.

Native Graphite, (*c.*)—A portion of the massive variety associated with (*a.*) It contains earthy matter and interspersed scales of mica, with grains of partially decomposed felspar.

Six grains treated as before, yielded; carbonic acid, 14·36 grs. This corresponds in 100 grs. of the graphite, to carbon, 65·4 grs.

In all these experiments the oxydation was completed in about thirty minutes.

Kish, (*a.*)—This material was in very thin crystalline plates, not acted on by the magnet.

Six grains in two successive experiments gave—first, carbonic acid, 20·50 grs.; second, carbonic acid, 20·42 grs. The mean of these results, 20·46 grs., corresponds in 100 grs. of the kish, to carbon, 93 grs.

Kish, (*b.*)—This specimen was in larger flakes, with adhering iron and slag. Before submitting it to experiment, it was digested for some hours in hydrochloric acid to remove the iron, and was then washed and dried. It still retained much adhering siliceous matter, as became evident in crushing it with the pestle.

Six grains in two successive experiments gave—first, carbonic acid, 16·58 grs.; second, carbonic acid, 16·65 grs. The mean of these numbers, 16·61, corresponds in 100 grs., to carbon, 75·5 grs.

Black Carbonaceous Sublimate.—This material was collected from the interior of a flue used for burning the native carburetted hydrogen, so extensively employed some years ago as a fuel, at many of the salt-works in the Kenawha Valley, Virginia. It is very light, of a spongy texture, harsh to the touch, hard enough where most compact to scratch glass, and of a deep black color externally, passing into greyish black within.

Finding by some preliminary experiments, that it resisted oxydation even *more powerfully than graphite,* we subjected it to still longer trituration with the silica than we had found necessary with the graphite, and we employed in the oxydation a somewhat greater excess of sulphuric acid than in the preceding cases. The evolution of CO_2 did not begin until the lamp had been applied for several minutes, and its progress was much slower than with the graphite, the complete oxydation requiring nearly an hour.

Six grains of this material, previously well calcined to remove moisture or other volatile matters, yielded carbonic acid, 21·62 grs.; corresponding in 100 grs. of the calcined sublimate, to carbon, 98·2 grs.

As a means of testing in some measure the accuracy of the process above described, the following experiments were made to determine the carbon of the graphite (*a*) and the black sublimate, by burning a weighed quantity of these substances in oxygen.

The apparatus employed for burning the graphite was a spacious platinum crucible, through the cover of which was passed a pipe connected with an oxygen gasometer so as to supply a gentle stream of this gas to the ignited materials. By previous trials, it was found that the black sublimate could be readily burned in a current of oxygen passed over it in a tube of refractory glass, and this method was accordingly used for its oxydation.

Before triturating the graphite with the silica, the latter was intensely ignited to drive off the trace of moisture which it had been found to contain. Twelve grains of graphite (*a*) thoroughly ground with the silica thus prepared, were exposed in the platinum crucible to a bright red heat, the interior being supplied continually with oxygen from the gasometer. In about fifty minutes the carbon of the graphite was entirely consumed. The residue had a faint brownish tint, while the unmixed silica similarly ignited, was found to retain its original whiteness almost unaltered. This slight colorarion of the former was doubtless due to the trace of iron present in the graphite.

The loss of weight sustained by the contents of the crucible, was 11·30 grs. Considered as due entirely to the burning of the carbon, this would give for the 100 grs. of graphite, carbon, 94·16 grains.

Twenty grains of the sublimate in coarse powder, weighed after strong calcination, were deposited in the trough of a bent slip of mica, and in this position, introduced into a tube of Bohemian glass, drawn to a small orifice at one end and adapted at the other to the pipe of the oxygen gasometer. After raising the material to a low red heat by a lamp applied beneath the portion next the gasometer, a *very gentle* current of oxygen was allowed to pass along the tube. A steady combustion without scintillation was thus maintained, which traveling slowly to the remote end of the carbonaceous matter in the mica trough, reduced the whole in a few minutes to a light greyish ash. The mica was then withdrawn, and the ash on weighing, amounted to 0·33 grains. It showed by tests a scarcely sensible trace of iron, and consisted almost wholly of silica.

Regarding the sublimate as made up of this and carbon—we have with 100 grs., earthy matter, 1·65 grs., and carbon, 98·45 grs.

Comparing now the results by the new oxydating process with those obtained by ignition in oxygen, we have,

	New Process.	Ignition.
Fibrous Graphite,	94·56	94·16
Black Sublimate,	98·29	98·45