$$Li_2C_2 + 2H_2O = 2LiOH + C_2H_2$$
$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$$

2. Decomposed by hydrochloric acid, giving acetylene.

$$Ag_2C_2 + 2HCl = 2AgCl + C_2H_2.$$

So also copper, mercury and gold (?) acetylides.

3. Decomposed by water yielding methane: aluminum and glucinum carbides.

$$C_3Al_4 + 12H_2O = 3CH_4 + 2Al_2(OH)_6.$$

4. Decomposed by water giving methane and hydrogen: manganese carbide.

$$Mn_3C + 6H_2O = 3Mn(OH)_2 + CH_4 + H_2.$$

5. Decomposed by water giving mixtures of acetylene, ethylene, methane and hydrogen: yttrium, lanthanum and thorium carbides.

6. Decomposed by water giving beside the above volatile products a residue of liquid and solid hydrocarbons; lanthanum, cerium and uranium carbides.

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## AN EXAMINATION OF COMMERCIAL FLOUR.[1]

BY HENRY KRAEMER.

Received April 24, 1899.

IT is now nearly two years since Professor J. U. Lloyd asked the writer to take up the microscopical examination of flour and its adulterants, especially with the view of applying a method, already proposed by the author, at the meeting of the American Pharmaceutical Association in 1894,[2] for the quantitative determination of corn-meal in flour. A careful preliminary examination of the flour and corn-meal upon the market soon indicated that a detailed study of other cereals, as well as of starch grains, was necessary before reliable and practical results could be obtained. The work upon the starch grain itself was presented, at least in part, in a paper on "The Study of Starch Grains, etc.," to the Pure Food and Drug Congress, January, 1899. It is not necessary here to dwell either upon this study or upon the results of the morphological study of the cereals, as Tschirch and Oesterle have published monographs of

[1] Presented at the joint meeting of the Cincinnati Section with the Columbus Section, University of Cincinnati, April 15, 1899.

[2] Proceedings of American Pharmaceutical Association, 1894; and *Am. J. Pharm.*, 1894.

the important anatomical features of all the prominent cereals in their "Anatomischer Atlas (Lief. 9–11). Furthermore it was found necessary to consider the various commercial varieties of wheat, the different processes of manufacture, and the by-products and their possible utilization, as well. And in this connection it may be stated that most of the information of this character is quite well known among the more intelligent and progressive millers.[1]

## GENERAL EXAMINATION.

The flour examined by the author represented all grades from those selling as low as $1.50 per barrel to the very highest grades, and included the various brands known as "spring wheat," "winter wheat," "Patents," various "blends," "bakers," etc. The first step in an examination of this kind is to determine the grade of the sample under consideration. The following is the procedure then followed by the author:

1. The color test is very useful and may be employed in a dry or wet way. The latter method, however, is preferable and appears to be the one most generally employed by millers as being reliable. In the dry method the samples of flour are placed side by side on a dark-colored board, each sample occupying a space of about one by three inches and less than one-fourth inch in depth. A comparison of unknown samples with a known standard is thus readily made. In the wet method the same procedure is followed, only the board upon which the samples are arranged, is immersed in pure or distilled water at a temperature not exceeding 35° C. In the course of an hour or longer the samples develop a more or less pronounced color according to the grades represented. The author prefers the use of a colorless glass instead of the colored board, as the color effect may be varied by placing the glass upon either a dark or a light surface.

2. The "doughing test" is a very serviceable one and is employed quite extensively by brokers and commission houses. Of course the value of this test is largely dependent upon the personal element or the experience which the operator has had. In the writer's experience the following method gives results which,

[1] A very instructive article of a popular character on this subject, appeared in the March number of the *Cosmopolitan*.

though not conclusive in themselves, are fairly characteristic. On mixing from fourteen to fifteen grams of flour with ten cc. of water at the ordinary temperature, a dough is obtained which is quite cohesive and may be handled without sticking to the apparatus employed. On cool and dry days apparently less flour is required to procure a mass which is not sticky than when the temperature is warmer and the humidity greater. It was thought by the author for some time that the lower grade flours did not require as large a proportion of water to form a dough as the better grades, but the results obtained on treating numerous commercial samples in the foregoing manner would indicate that more likely the opposite is true. However this may be, the dough gives certain prominent characteristics. One of the most prominent, besides that of color, is the firmness of texture which results in some cases. In the better grade flours there results a lighter dough, which is quite elastic, whereas the lower grade flours produce a dough which is more compact.

3. The "gluten" test, which depends upon the washing out of the starch from the mass of dough, is well known to chemists. As to what gluten really is, seems not to be well established. By some writers the gluten is said to be contained in the layer of cells immediately under the pericarp or coat of the grain of wheat. Other authorities claim, however, that in this layer we find aleurone grains and oil and that the gluten is contained rather in the endosperm or reserve cells containing the starch. They ascribe to the protoplasmic threads of these cells the property of gluten. Both are nitrogenous in character and give the same reactions with Millon's reagent for such substances.

The importance of the gluten test appears to depend, according to the writer's experience, more upon its use as a qualitative than as a quantitative test. The physical characters noted above in the examination of the dough, are also found to belong to the gluten mass, obtained as stated by washing the dough with water. A microscopical examination of this glutenous mass furnishes probably the best means for determining the extent to which the flour has been refined. In the better grades of flour we find an almost transparent, delicate, fibrous mass, in which numerous starch grains are imbedded. There are, however, few or none of the hairs of the beard of the grain of wheat and none of the fragments of the pericarp or coat of the grain. In the poorer samples of flour the hairs and fragments of the pericarp are found to increase in proportion to the decrease of the specimens in quality. From this examination it is very apparent that what is reckoned as gluten may consist of a variety of substances, besides more or less starch, as it is almost impossible to remove the last portions of the latter substance.

It is doubtful whether, as commonly reported, the baker's flours contain more gluten than the patent and other more refined flours of the modern mills. That the lower grades of flour require a greater proportion of water to form a cohesive dough is believed by the author to be due to the presence of a larger proportion of oil in these grades, the oil being contained as above stated in the so-called "gluten" layer along with the aleurone grains. Furthermore, the large quantity of gluten reported as being present in the lower grades of flour is made up, as shown above, of various foreign substances, in addition to the gluten itself.

4. The "baking" test is regarded by some manufacturers and dealers to be the most reliable of any, In determining the grade of a flour test by this the following data are taken into consideration: Weight of flour used, amount of water, yeast and salt, temperature, time required, size and weight of finished loaf, and appearance of same on cutting.

5. The "paste" test may have some significance in determining the quality of flour. The writer finds that if one gram of flour is well mixed with fifteen cc. of water and then gradually heated to boiling, with constant stirring, and allowed to boil for one minute, that the higher grades of flour give a paste which on cooling will scarcely flow at all, whereas the lower grades give a paste which is more liquid in form. In addition the paste in the former case is of a smoother consistency, the latter being characterized by a more or less granular consistency.

6. *Odor.*—Flour having a rather characteristic odor of its own, the presence of foreign substances in it has often been determined by the mere addition of boiling water to the sample. While making some experiments in heating various cereals in glycerin, a very marked odor was detected in a solution contain-

ing corn-meal. This was so pronounced and characteristic that this method was employed for determining the presence of corn-meal in flour. The *modus operandi* is as follows: One gram of flour is mixed with about ten to fifteen cc. of nearly anhydrous glycerin and heated to boiling for a few minutes. If corn-meal be present, an odor similar to that of popped corn is developed. As small an admixture as five per cent. of corn-meal may be detected in this way.

7. In addition to the more or less characteristic general tests above enumerated for determining the value of a flour, the sense of touch may likewise be utilized for this purpose. This method, however, is of value only in the hands of one whose experience has been considerable and whose sense of touch has been especially developed in this direction.

## QUALITATIVE EXAMINATION.

The general examination as outlined indicates whether a flour is good, medium, or poor in quality. The more refined flours consist almost entirely of starch grains and a very delicate fibrous material. The cheaper flours contain in addition fragments of the thick-walled cells of the so-called "gluten layer," characteristic long thick-walled one-celled hairs of the beard of the wheat grain and also fragments of the pericarp or coat of the grain. In the still lower grades these tissues are present to a still greater extent.

The main object of this paper being to determine admixtures of corn-meal and flour, it may be stated that this subject must be approached with considerabe caution, as this work[1] is based for the most part upon a comparison of the starch grains of corn and wheat. While many of the starch grains of both corn and wheat are quite characteristic, it must be stated, on the other hand, that a large proportion of them so closely resemble each other that in an admixture it is oftentimes practically impossible to distinguish the one class from the other by the methods ordinarily employed. In order to obtain conclusive results, it is necessary that a special micro-physical and micro-chemical study of these starch grains be made. It is only the micro-chemical part of this work that can be referred to at the present time. The following reagents were used for this purpose and the action of them upon the starch grains of wheat, corn, and potato, was studied for the purpose of comparison :

1. Chloral iodine + iodine solution ; of each equal parts.
2. Chlor-zinc-iodide solution.
3. Chloral solution (saturated), water and glycerin ; of each three and three-tenths parts. To this solution as much iodine is added as the solution will take up.
4. Calcium nitrate solution (thirty per cent.).
5. Chromic acid solution (fifteen per cent.).
6. Saliva.
7. Taka-diastase (saturated solution).
8. Silver nitrate solution (two per cent.).
9. Sulphuric acid (C. P. acid ninety parts, water ten parts).
10. Sodium acetate solution (fifty per cent.).
11. Potassium hydroxide solution (one-tenth per cent.).
12. Potassium nitrate solution (saturated).
13. Potassium phosphate solution (saturated).
14. Tannin solution.
15. Hydrochloric acid (five per cent.).
16. Water.

*Wheat Starch.*—Chloral-iodine + iodine solution (No. 1) causes the grains to become at first uniformly blue in color ; swelling of the grains soon takes place and finally alternate light blue and blue layers are observed. Chlor-zinc-iodide (No. 2) behaves similarly to the preceding reagent. Chloral and glycerin solution (No. 3) behaves similarly to No. 1, but the grain is not colored and the lacunæ or fissures are more pronounced. Calcium nitrate (No. 4) produces in fifteen minutes a strong corrosion of some of the grains, and those not acted upon by the reagent in this manner swell in one hour very perceptibly, then show a "tricheten-like"[1] development and in five hours swell enormously and finally burst. Chromic acid (No. 5) produces a similar effect upon the grains, but appears to be more pronounced in its action. Saliva (No. 6) causes in some grains the development of prominent radiations and lamellæ, in others a tricheten-like structure is developed ; in five hours the grains give indications of corrosion, which in the

[1] Arthur Meyer cousiders the starch grain to be made up of alternate layers of two kinds of acicular crystals (which he calls "tricheten").

course of seventeen to twenty-four hours is very pronounced. Taka-diastase (No. 7) on the other hand, acts very slowly in comparison. In five hours there is little or no effect observable, the tricheten-like structure developing after this length of time and corrosion finally taking place. Silver nitrate (No. 8) has but little action upon the grains at first, in five hours the tricheten-like development appears, and later the grains swell and disintegrate. Sulphuric acid (No. 9) acts almost immediately, causes the grains to become nearly transparent and irregular in outline, and a rapid solution takes place. Sodium acetate (No. 10) causes some of the grains, in the course of five hours, to swell and others to become very much corroded. Potassium hydroxide (No. 11) produces very soon a swelling and rupture of some of the grains and in others the development of a prominent tricheten-like structure, and finally in both a slow corrosion. Potassium nitrate (No. 12) causes almost immediately a swelling and rupture of the grains, or a strong corrosion. Potassium phosphate (No. 13) produces prominent fissures with the subsequent development of rather numerous tricheten-like layers in some grains, in others there is a swelling and rupture of the grains, with finally a gradual corrosive action on both. Tannin (No. 14) produces a swelling of the grains, together with the development of rather large irregular lacunæ, and in five hours the grains become very much swollen and of irregular shape, after which disintegration and solution takes place. Hydrochloric acid (No. 15) causes the appearance of prominent tricheten in some of the grains in a few hours, in others there is a tendency to swell, and both kinds finally divide into two or more parts. Water (No. 16) at a temperature between 50° and 70° C. produces a marked effect upon the grains; those digested at a temperature between 50° and 55° C. for several hours, are swollen, and in many cases are even ruptured; at 60° C. they show a prominent tricheten-like structure, which is scarcely visible at 65° C., and after digestion at 70° C. for one hour the grains become very irregular and swollen and are apparently not further effected by a temperature between 70° and 95° C.

*Corn Starch.*—Chloral-iodine + iodine solution (No. 1) causes some of the grains to swell in five hours and others to show a tricheten arrangement of the layers; the grains do not appear to be swollen to the extent that the wheat grains are, and therefore show apparently a deeper color with the iodine. Chlor-zinc-iodide (No. 2) brings out immediately the fissure or point of growth, which is in marked contrast to the wheat starch; in the course of several hours the grains swell at one end, the portion showing the swelling becomes light blue, and finally almost colorless, while the other portion remains of a deep blue color; some of the grains finally disintegrate into several portions. Chloral and glycerin (No. 3) causes the appearance of lenticular, somewhat irregular, or more or less star-shaped and prominent lacunæ or fissures, and in the course of twenty-four hours in some grains prominent radiations are developed, whereas in others a marked swelling takes place. Calcium nitrate (No. 4) makes the point of growth more visible as with previous reagents, then strong radiations or a tricheten-like structure develops in some grains, whereas in other grains the fissures develop into large radiating canals, which extend to the margin of the grain, the swelling continuing so that in five hours only the outline of the grain is visible. Chromic acid (No. 5) causes a prominent swelling of the more or less star-shaped point of growth, which continues to such an extent in some cases as to produce a rupture of the grain at one of the angles; in other cases there are numerous radiations, or a tricheten-like structure, developed around the swollen fissures, which finally disappear as the grain swells and breaks down. Saliva (No. 6) acts upon the grain very much like chromic acid and calcium nitrate, only instead of a swelling of the grain we have a rather slow corrosion in the course of forty-eight hours following the pronounced development of fissures. Taka-diastase behaves like saliva, only the corrosive action is more rapid. Silver nitrate (No. 8) causes the formation of prominent and angular fissures, which become more or less circular in outline, and near the periphery prominent radiations may develop. Sulphuric acid (No. 9) produces in some of the grains marked development of an angular fissure which becomes circular or radiating in outline, whereas in others a corrosive action appears to begin at the periphery of the grain, followed by gradual solution of the entire grain. Sodium acetate (No. 10) behaves very much like calcium nitrate. Potassium hydroxide (No. 11) acts similarly on the grain to calcium nitrate and sodium acetate. Potassium nitrate (No. 12) differs in its action on corn very markedly from that on wheat, in that there is a strong development of radiating fissures which extend in many cases to the periphery, whereas in wheat there is a more pronounced swelling of the grains and an irregular corrosive action. Potassium phosphate (No. 13) causes the development of a prominent lenticular, or star-shaped fissure, which increases in size and in seventeen to twenty-four hours there is a complete breaking-down of the grain. Tannin (No. 14) causes also the immediate production of prominent fissures which in five hours develop into large canals, or circular portions, and there is finally a separation of the grain into several parts. Hydrochloric acid (No. 15) causes in some cases the development of large star-shaped or lenticular fissures, and in other cases in the course of but twenty minutes there is a marked swelling of the grain at one point, which continues until disintegration takes place. Water (No. 16), between the temperature of 50° and 70° C., causes certain characteristic features to be developed; the grains when heated for one and a half hours at 50° C., develop in most cases a rather pronounced circular fissure, in other grains there may be a swelling or lenticular or star-shaped fissure; at 55°–60° C. the swelling of the grain is more pronounced, and at 65° C. the remainder of the grains show a marked one-layered tricheten-like structure; at 70° C. the markings have disappeared and the grains have become swollen to angular and irregular masses.

In comparing the results of the aforesaid experiments some general observations may be made. We find that we have at least two different kinds of starch grains in each class. The wheat starch grains are either (1) nearly spherical or elliptical in outline without any prominent point of growth, or (2) are characterized by a many-armed fissure looking like the stone cells in tea leaves. The corn-starch grains are either (1) four to six angled and possess a pronounced lenticular or star-shaped fissure, or (2) are nearly spherical with a more or less circular point of growth. Number one in each of these two classes may be said to represent the typical wheat starch and corn starch grain. The tricheten-like structure already referred to appears to be developed by the action of the reagent in less time and at lower temperatures in wheat grains than is required to produce this effect in the corn starch. Furthermore, a marked difference in size is manifest in the starch grains of corn and wheat when mounted in water and when swollen by the various reagents. Wheat starch grains when examined in water are one to forty-two microns in diameter, the typical grain for purposes of study being about seventeen microns in diameter; when swollen the grains range in diameter from three to seventy microns, the typical being about fifty-three microns. The starch grains of corn when examined in water are from one to twenty-one microns in diameter, the typical grain being about fourteen microns in diameter; when swollen the grains range in size from four to forty-four microns, the typical being about fifty-three microns in diameter.

## QUANTITATIVE EXAMINATION.

It is essential before making a quantitative microscopical examination of flour that a general and qualitative examination, as already described, be made. The author, as stated, in the preface of this paper, proposed some years ago a method for the valuation of powdered drugs and foods, by means of the microscope. This was subsequently elaborated in a paper published in 1897.[1] Inasmuch as the method used at that time is applicacable to the present work some of the most important details are here given.

(1) The same *reagents* and mounting media are employed in doing quantitative work as were considered in the qualitative examination of the flour.

(2) The quantity of flour to be examined by means of the microscope must represent the sample in every particular; in other words, the *sampling must be done properly* and in accordance with the methods used in the assay of ores. While the quantity to be examined may consist of but a few grams, it must thoroughly represent the lot of flour on which value is to be given.

(3) The amount of sample used in the examination is generally about $\frac{1}{256}$ gram (= 0.0039 gram = 0.06 grain). The quantity of flour may be weighed out, or, what is more con-

[1] See Proceedings of the American Pharmaceutical Association, 1897; also American Journal of Pharmacy, October, 1897.

venient, with practice, a gram is weighed out and divided with a spatula, as follows :

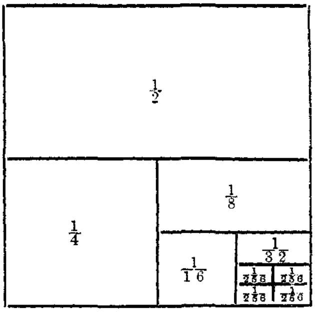


Fig. 1.

$\frac{1}{2} = 0.500$ gram.
$\frac{1}{4} = 0.250$ "
$\frac{1}{8} = 0.125$ "
$\frac{1}{16} = 0.0625$ "
$\frac{1}{32} = 0.03125$ "
$\frac{1}{128} = 0.0078$ "
$\frac{1}{256} = 0.0039$ "

(4) The cover-glasses used, whether round or square, *should be uniform in size and thickness* for comparison of the mounts of the standards with those of the specimen to be tested.

(5) The *amount of reagent* employed in making a mount must be just sufficient to float the cover-glass, and as few air-bubbles as possible are permitted to be formed.

(6) *A homogeneous mixture* of sample with reagent must be formed before the cover-glass is put down. This is best done by taking the edge of the cover-glass in a pair of forceps and distributing the powder in the mounting media or reagent.

(7) After the mount has been made and the sample examined previously qualitatively, the quantitative estimation of the powder is made. This is based on one or more of the structures or constituents that are characteristic of the sample.

When samples of lower grades of flour are examined the fragments of the pericarp, thick-walled cells of the so-called "gluten layer" and the characteristic hairs of the beard are the structures discerned. In the examination of flour containing corn-meal, the typical starch grains of the latter are selected as a basis for the determination.

The employment of the ocular micrometer, ruled in 100 square millimeters (proposed by the author in 1894), or of the ordinary ocular micrometer (proposed by the author in 1897), is not applicable in the examination of flour as the typical corn starch grains and tissues found in inferior grades of flour are not sufficiently numerous to warrant this procedure. The method best adapted for the examination of these grades consists in the employment of either the high or low power objective and counting the number of typical starch grains or characteristic tissues which are found in examining five portions of the mount, as indicated by the diagram.

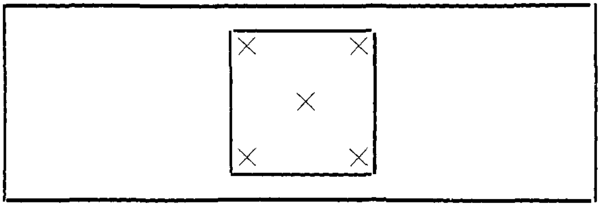

Fig. 2.

When the flour does not contain any corn-meal the low power objective is employed. When corn-meal is present the high power objective (one-fourth to one-eighth inch) is necessary.

(8) *The number of mounts* to be made of the standard and the sample under examination should generally not be less than twelve each. But as two to three mounts can be made upon the same slide, from four to six slides only are necessary for each sample.

(9) If the sample is found to be a mixture, a similar compound, representing the proportions found, should be made up, and the powder under investigation be compared with it.

It is thus apparent that the quantitative results are wholly dependent upon comparisons of an unknown with a known sample. The conditions must be nearly the same in both. The sampling must be done similarly; the same amount of sample must be used in both cases, and no more reagent or mounting media should be used than is necessary to hold the cover-glass without any air being impinged. The same microscope and objectives, as well as other conditions, must be employed to secure even *approximate results*, as this is *all that can be expected at present.*

In the examination of low-grade flours when there is no adulteration with corn-meal, it is not possible to obtain quantitative values, save in terms of some other samples, the market value of which and the extent of refining are known. In the consideration of samples of flour containing corn-meal we find a different condition. Here the quantitative valuation in terms of corn-meal is based upon the comparison of the unknown samples with prepared samples containing a definite percentage of corn-meal. The count is based upon the number of typical angular corn starch grains with prominent fissures found in the five places of each of twelve mounts, as indicated in Fig. 2. Samples of flour containing from five to ten per cent. of corn-meal have on the average from two to three typical corn starch grains in each mount. When the adulteration varies from ten to twelve per cent. the average number of these starch grains is increased from four to six. In samples containing twenty-five per cent. of corn-meal the average number of typical grains increases to seven, etc., but as the adulteration of commercial flours, according to the author's experience, does not exceed ten to twenty per cent., it is not necessary to proceed further in this direction.

CLASSIFICATION.

From the results of the following experiments a classification of the commercial flours may be made as follows:

I. Those that produce a stiff and cohesive dough in the proportion of fourteen to fifteen grams of flour to ten cc. of water; as, for example, a good spring wheat flour.

II. Those that do not produce a stiff and cohesive dough in the proportion of fourteen to fifteen grams of flour to ten cc. of water.

These may be further divided into the following subclasses:

A. Those that form a smooth, jelly-like paste upon boiling one gram of flour with fifteen cc. of water for about one minute; as, good winter wheat and some of the blended flours.

B. Those in which a more or less granular or liquid paste results. This subclass may be further sub-divided into:

(*a*) Those which give off an odor of roasting corn when heated in glycerin to boiling for a few minutes, as samples containing corn-meal.

(*b*) Those that do not give off an odor of roasted corn when heated to boiling with glycerin, as lower grades of flour.

The quality of these flours may be still further determined by a microscopic examination of either the flour or the gluten mass after removal of the starch, when the presence of fungi and other foreign substances are revealed.

It appears that in certain sections of the country the adulteration of flour, as of other powdered commercial products, is still practiced, yet it may be said that as a rule the article as found in the eastern markets, represents a higher grade of product than has formerly been reported.

The investigations of the writer indicate certain profitable lines of work which are of immediate practical value, and it must be said that much still remains to be done, particularly in the micro-physical examination of the different starches; and the author is of the opinion that as much useful knowledge will be secured by the utilization of the polariscope in this field of work, as has already been disclosed by other methods, the usefulness of this instrument having been demonstrated in the examination of the products made from plant and other fibers.

The author is indebted to Professor Higley, of Northwestern University, and to J. W. Dietrich, of Galesburg, Mo., for assistance in procuring samples; and to Miss Florence Yaple, of the Philadelphia College of Pharmacy, for the performance of much experimental work in the course of the investigation.

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[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 10.]

## PREPARATION OF GRAPHITOIDAL SILICON.[1]

BY FREDERICK S. HYDE.

Received April 12, 1899.

THE analogy between silicon and carbon in their allotropic modifications, especially the graphitic, and the existence of a crystalline compound of silicon and carbon, known as carborundum, have tended to create doubt as to the purity of graphitoidal silicon, yet the production of the latter seems to be based on reactions favoring the exclusion of carbon.

The usual methods involve the reduction of potassium-silicofluoride with aluminum or metallic sodium; or the reduction of pulverized white sand with magnesium powder.

The method submitted depends on the reduction of finely pul-

[1] Read at the meeting of the New York Section of the American Chemical Society, March 10, 1899.