The preferred procedure is as follows: to 50 cc. of the cold neutral solution add 25 cc. of concentrated hydrochloric acid and 5 cc. of freshly filtered stannous chloride solution, containing 1.125 g. of $SnCl_2 \cdot 2H_2O$ per cc., dissolved in hydrochloric acid (sp. gr. 1.09) and kept over metallic tin. Stir and let settle (or centrifuge). Settling is usually complete in thirty minutes to an hour. Filter through a filtering crucible, previously dried with acetone and dry air, wash with 1:1 hydrochloric acid to prevent hydrolysis of tin salts, then with water and finally with acetone. Dry for five minutes by sucking through the crucible air dried by calcium chloride and weigh. The volatility correction in this method, determined from the average of twenty analyses, is +1.0 mg.—somewhat lower than in the hydrazine method. This may be due to the larger size of the particles. The results are shown in Table III.

## Summary

1. Conditions are given for the accurate gravimetric determination of mercury after reduction to metal by hydrazine in ammoniacal solution or by stannous chloride in hydrochloric acid solution.

2. In the latter method iron, cadmium, bismuth, copper, lead, antimony, nitrate and sulfate do not interfere.

3. There is always a definite constant loss due only to volatilization of mercury during filtration and drying, for which an accurate correction can be made.

4. A rapid method of drying is described, using acetone and dry air.

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# THE SODIUM PEROXIDE–CARBON FUSION FOR THE DECOMPOSITION OF REFRACTORIES

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The usual methods for decomposing refractory materials are far from being ideal, in that they require considerable manipulatory skill, are time-consuming, and frequently do not effect complete decomposition in a single treatment; in fact, for some commercial refractories several types of fusions must be used in succession to obtain this result. Alkaline and acid fusions are frequently carried out in platinum crucibles, entailing considerable expense where a number of analyses must be carried on at once, while nickel, iron or porcelain crucibles are usually badly attacked under similar circumstances. The temperatures obtainable in a fusion are in general limited to those furnished by a gas flame or an electric heating element, commonly not above 1100°. In view of these considerations, a method of fusion which would eliminate some of the objections mentioned is desirable.

Sodium peroxide has been used in the decomposition and analysis of organic compounds for a number of years.[1] In 1925 W. F. Muehlberg[2] described "An Explosion Method for Peroxide Fusion," which showed great possibilities. The metal crucibles would last indefinitely and a number of samples could be fused nearly simultaneously and with a minimum of effort. The cooled melt separated from the crucible very readily and its acidified solution was always clear. The application of the method to the analysis of ferrosilicon was outlined. In a private communication Mr. Muehlberg kindly suggested several lines of further investigation; namely, that aluminum oxide and corundum might be studied with a view to extending the possibilities of this type of fusion. Previous to the work of Muehlberg, we have found no reference to the use of sodium peroxide with sugar carbon for the decomposition of inorganic compounds. From a quantitative aspect it seemed desirable to investigate the efficacy of this method of fusion in the case of a variety of highly refractory materials, such as alundum, cassiterite, zircon, rutile, beryl, mullite, carborundum, graphite, etc.

The following method of study was adopted: (1) to prepare a series of mixtures of sodium peroxide with sugar carbon in varying proportions, and after explosion of these mixtures to determine, if possible, the most advantageous ratio of the components; (2) to use this mixture with an analyzed sample of a refractory material; to vary the proportion of fusion mixture to sample in an effort to determine the proper ratio of mixture to sample, as well as the proper method of mixing, and to determine the amount of unfused residue in each case; (3) to try other organic substances in place of sugar carbon; (4) to fuse a variety of highly refractory materials and in each case to determine the amount of unfused residue, as well as to determine whether or not the unfused material is changed, *i. e.*, whether or not there is any selective action by the sodium peroxide; (5) to determine the maximum temperatures obtained in the case of representative fusions.

## Experimental Work

An aluminum tray 12 × 6 × 1 inches was prepared for cooling the crucibles after a fusion. Fitting over the top of this tray was a metal plate with six holes, $1^5/_8$ inches in diameter. A 60-cc. nickel crucible placed in one of the holes would be held firmly in position while resting on the bottom of the tray. Cold water was allowed to run into the bottom of the tray and overflowed at the top.

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[1] In particular, by Pringsheim, *Ber.*, **36**, 4244 (1903); von Konek, *Z. angew. Chem.*, **16**, 516 (1903); Pringsheim, *Chem. News*, **91**, 215 (1905); Parr, *J. Ind. Eng. Chem.*, **14**, 681 (1922); Hein, Hoyer and Klar, *Z. anal. Chem.*, **75**, 161 (1928).

[2] Muehlberg, *Ind. Eng. Chem.*, **17**, 690 (1925).

To obtain a uniform sample of sodium peroxide, the contents of six cans of approximately 150 g. each were thoroughly mixed and placed in glass-stoppered bottles. The purity of the sodium peroxide was tested by acidifying with hydrochloric acid and dehydrating to determine silica. A 15-g. sample thus yielded a residue of 0.003 g.

The sugar carbon used was from Eimer and Amend, bearing the note "prepared from cane sugar." It was somewhat lumpy and was ground in an agate mortar until it passed through a 100-mesh screen. It was noted that when the carbon had been ground to about 50-mesh it assumed a flaky character, resembling that of graphite. This condition made subsequent grinding a tedious operation. Using an automatic grinding apparatus, about 200 g. of 100-mesh carbon was prepared. The purity of the sugar carbon was tested by the ignition of several 2-g. samples in a muffle furnace, addition to the residue of a mixture of sulfuric and hydrofluoric acids, evaporation and ignition. Three samples thus gave residues after the first ignition of 0.0041, 0.0041 and 0.0044 g., respectively. These residues proved to be practically pure silica when subjected to the hydrofluoric acid treatment.

Seven mixtures of sodium peroxide and sugar carbon were prepared, containing, for each 150 g. of peroxide, 7.5, 8.0, 8.5, 9.0, 9.5, 10.0 and 11.0 g. of carbon, respectively. In a preliminary experiment 15 g. of each of these mixtures was fired under identical conditions with no added substance present, the method of firing being as follows. The mixture was weighed into a 60-cc. nickel crucible, then tamped down gently with a glass rod flattened at one end. The crucible was placed in the metal trough with cold tap water circulating in it, and the mixture was fired by means of the glowing end of a piece of cotton string, inserted through a small hole in the cover of the crucible. The speed of the combustion process increased with increasing proportion of carbon present in the mixture from a slow, but complete combustion, to a very rapid one. The solid mass left in the crucible after the fusion was readily transferred from the crucible to a beaker by tapping and about 60 cc. of cold water was added. After the resulting reaction was complete, the solution was diluted to about 300 cc., cooled, acidified with hydrochloric acid and filtered; the residue was washed with hot water, ignited and weighed. The residues so obtained from the seven mixtures, run in duplicate, varied from 0.0006 to 0.0015 g., and no one of the mixtures could be said to be superior to any other.

In order to determine which of the fusion mixtures was most satisfactory for general use, an analyzed sample of feldspar prepared by the Bureau of Standards and marked "sample 70" was selected, particularly because of its high silica content (66.66% $SiO_2$), and because it was not especially difficult to decompose. A one-gram sample of this feldspar was mixed with 15 g. of each of the fusion mixtures, care being taken to prevent the sample from coming into contact with the sides of the crucible. This was accomplished by transferring the weighed sample into a conical depression made in the fusion mixture and carefully stirring the sample and fusion mixture with a small spatula, while not disturbing the lining on the sides of the crucible. The entire crucible contents were finally tamped down with the flattened end of a glass stirring rod. On ignition of the seven samples thus prepared, the first three, containing the lowest proportions of sugar carbon, were found unsatisfactory because the reaction was too slow and incomplete; the seventh was discarded as being too rapid for personal safety. The range of mixtures was thus narrowed to the fourth, fifth and sixth, and while no considerable difference in the behavior of these three was noted, Mixture 6, containing 150 g. of sodium peroxide to 10.0 g. of sugar carbon was adopted for later use as being the most satisfactory from the point of view of completeness and speed of reaction and ease of preparation.

In the treatment of the contents of the crucible after fusion with water and subsequently with hydrochloric acid, in each case a large quantity of silicic acid gel formed, the filtration of which in the usual way would have been tedious. To obviate this difficulty, the following expedient was employed. After the usual 60 cc. of cold water had been added to the fusion product to decompose the unchanged sodium peroxide, water was added to a volume of about 400 cc. and the whole allowed to stand; after settling, the supernatant liquid was decanted and the solution again diluted to 400 cc. and allowed to settle. After the fourth decantation the solution was acidified and filtered, and the residue washed, ignited in platinum and weighed. Much time was saved by this procedure, inasmuch as the greater part of the sodium silicate had been eliminated before the solution was acidified, thus eliminating the necessity of filtering a gelatinous precipitate. In three typical fusions, using one gram of feldspar with 15 g. of fusion mixture, by the above treatment, residues of 0.0079, 0.0087 and 0.0073 g. were obtained upon ignition. To each of these in platinum crucibles a few drops of concentrated sulfuric acid and about 1 cc. of hydrofluoric acid were added, the whole evaporated to dryness and ignited. Losses of 0.0024, 0.0040 and 0.0015 g., respectively, were observed, thus indicating that the greater part of the unfused residues consisted of undecomposed feldspar.

This conclusion was wholly confirmed by examination of the residues obtained above, as well as the original sample, with a petrographic microscope; the unfused material showed the typical twinning of crystals of feldspar, and possessed the same refractive index as the original material. Whereas the grains of the original material showed sharp broken edges, the grains of the unfused residue had rounded ends with no sharp edges, indicating that incipient fusion by the sodium peroxide treatment had occurred.

It was now obviously a question of determining how best to reduce the amount of unfused residue to a minimum. First, very thorough grinding of the sample in agate was tried, until all the sample would pass through bolting cloth, approximately 100-mesh. The amount of residue obtained from a one-gram sample after fusion and subsequent treatment as already described—0.0082 g.—showed that grinding alone would not suffice to bring about complete fusion.

Various expedients were tried in modifying the method of mixing the sample and fusion mixture, both within and outside the crucible, and the ratio of mixture to sample was raised to 25:1, but the unfused residues remained unsatisfactorily large, until it was discovered that the cause of the large residues was due to spattering of material during fusion on to the sides and cover of the crucible. Thus, it was found, when the spattered material and the solid fused mass in the crucible were separately treated after fusion, that approximately 80% of the residue came from the spatterings, the rest—about 1 mg.—from the solid lump. The spattering could not be eliminated entirely by any of the several expedients tried, although a covering of about 5 g. of sodium carbonate applied to the contents of the crucible before firing was found to reduce this considerably. Thus, using a one-gram sample of feldspar in the usual method of procedure, but employing the sodium carbonate covering, three samples gave residues as follows: (a) from the solid mass in the crucible, 0.0004, 0.0008 and 0.0005 g.; and (b) from the spatterings, 0.0038, 0.0024 and 0.0021 g., respectively.

Several mixtures of organic compounds with sodium peroxide were tried with a view to determining whether or not the carbon might be replaced by a compound, and the necessity of grinding the carbon thus eliminated; but of the substances tried, in varying proportions, with the peroxide—benzoic acid, oxalic acid and tartaric acid—none gave as satisfactory results as the ground sugar carbon. It is possible that certain pure, solid hydrocarbons, such as triphenylmethane, would prove to be satisfactory substitutes for the carbon, but further work along these lines was not attempted.

It was thought desirable to determine, at least approximately, the maximum temperature attained in this method of fusion. For this purpose the use of a thermocouple or optical pyrometer seemed impracticable, as the high temperature obtained lasts but a few seconds. Strips of silver foil and copper foil melted readily in the fusion mixture so that a temperature of at least 1100° was indicated. By the use of flake graphite in place of sugar carbon the combustion progressed more slowly, requiring about thirty seconds for completion, so that an optical pyrometer could be employed. With this instrument typical fusion mixtures on firing showed temperatures of approximately 1450°. It seems probable that with the faster burning charcoal temperatures considerably in excess of this are attained.

The following highly refractory materials, after grinding in agate, were now fused in succession, employing the usual procedure outlined above: 1, fused kaolin brick; 2, ignited crucible, largely zirconium oxide; 3, sipylite, chiefly erbium columbate; 4, commercial product of fused alumina and magnesia; 5, commercial product of fused alumina and silica; 6, alundum; 7, cassiterite; 8, corundum; 9, rutile; 10, zircon concentrates; 11, beryl; 12, ilmenite; 13, mullite, a commercial product of fused alumina and silica; 14, carborundum; 15, flake graphite.

In certain cases grinding of the sample to 100-mesh was found desirable, so that residues of only a few milligrams should result after fusion and subsequent treatment. For example, one-gram samples of alundum and corundum gave the following residues.

| | | Without careful grinding of sample, g. | Sample ground to pass 100 mesh, g. |
|---|---|---|---|
| I Alumina | Residue from fusion | 0.0020 | 0.0016 |
| | Residue from spattering | .0020 | .0005 |
| II Corundum | Residue from fusion | .0073 | .0010 |
| | Residue from spattering | .0058 | .0004 |

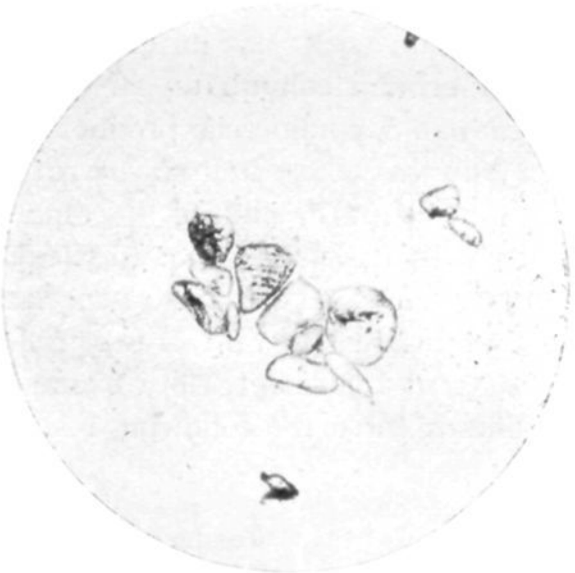
In nearly all cases, when careful grinding was employed, the total residue obtained from a one-gram sample did not exceed 0.0025 g. and was usually much less than this.

In the case of the carborundum sample, the procedure was modified in order that the reaction might not be too violent. About 10 g. of fusion mixture was placed in the bottom of the crucible and above it 10 g. of sodium peroxide was introduced, into which the 0.5-g. sample of carborundum (100-mesh) was stirred. The whole was covered with about 5 g. of fusion mixture and fired. The results obtained were very satisfactory.

In the case of the graphite, the sugar carbon was entirely omitted and the one-gram sample mixed directly with 15 g. of sodium peroxide. The residue after acidification was filtered through a Gooch crucible instead of being ignited in the muffle furnace, since in the latter the graphite residue was observed to burn down to an ash.

The fact that the sodium peroxide–carbon fusion does not have a selective action on the refractories studied was determined by microscopic examination of the crystal grains, before and after fusion. For example, Sample 13, mullite, before and after fusion gave the appearance seen in the photomicrographs. Before fusion the grains were not uniform in size and showed sharp edges—in the sample shown in the photomicrograph the smaller grains were washed away by decantation and only the larger ones remained; after fusion, the fragments of residue obtained were more nearly uniform in size and the edges appeared rounded—in preparing the photograph of the fused material the decanting of the lighter particles was not carried out. Consequently, the fusion appears to have entirely consumed the smallest particles and uniformly eroded the surfaces of the larger ones—facts that indicate no selective action on the part of the fusion medium. In calculating the results of an analysis, it, therefore, would seem to be justifiable merely to subtract the weight of residue from that of the original sample.

Before fusion.



After fusion.

## Summary

A quantitative study of the sodium peroxide–carbon method of fusion has been made in the case of fifteen highly refractory materials, including both naturally occurring minerals and artificial products. The results show that, properly executed, this fusion may well replace any of the customary methods for the decomposition of refractories, being more complete in many cases, and far superior in point of speed and ease of manipulation; being carried out in nickel, it obviates the need of platinum crucibles. No loss in weight of the nickel crucible is detected after repeated use.

Details are given for the proper method of procedure in preparing the sample and the fusion mixture, as well as the proper proportions of mixture to sample, the mode of charging, firing and cooling the crucible and the subsequent treatment of the fusion product.

It is shown that the unfused residue from a one-gram sample, ground to at least 100-mesh, need not exceed two milligrams, and that this small residue consists of particles of the original sample and, therefore, may be subtracted from the original weight.

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