

By C. F. Metz

NOV 1948
OSTI
1000-11

In the specifications for the beryllium metal being used at installation as the New Rocky Flats Plant a minimum Beryllium assay of 98.0 percent is required. The major impurity in beryllium is oxygen, which presumably is present as beryllium oxide (BeO), and concentrations of about 1.5 percent beryllium oxide or about 1.5 percent oxygen are common. The main analytical problem then is to measure the beryllium in the material or to determine impurities present and estimate the beryllium content by difference. Neither approach to the analysis is simple or entirely satisfactory. The assay methods are limited in number and are mainly empirical in nature. The difficulties experienced in determining oxygen in beryllium are manifold, as will be pointed out later.

Assay Methods

The two most widely-used methods are the gravimetric determination as beryllium oxide and the empirical volumetric titration method. In the gravimetric determination, beryllium hydroxide is precipitated by adding ammonium hydroxide to a solution of the sample to which EDTA has been added to complex metallic impurities. The hydroxide precipitate is dried, ignited, and weighed as BeO . Impurities in the oxide are determined (spectrographically and by other methods) and the necessary corrections are made. In addition to uncertainties because of the calculated corrections, the proper ignition temperature is not fully established and improper ignition may lead to poor results. At Rocky Flats Plant the hydroxide is ignited at 900 to 975°C., then the oxide cake is broken up mechanically and ignited for 2 hours at 1200°C. The British reported that a study was being made to determine the optimum ignition temperature. They found that temperatures above about 1200°C. were detrimental but an optimum temperature had not yet been established.

In the volumetric method the hydrogen gas liberated from beryllium hydroxide when the beryllium is complexed with fluoride is titrated with sulfuric acid, using a glass-calomel electrode system to detect the endpoint. The acid must be standardized daily to minimize the analytical error that is introduced from day to day. As is the case in the gravimetric determination, impurities, notably aluminum, must be determined and a correction applied.

Rocky Flats Plant and the British use the gravimetric method (which is also the method used by the majority of beryllium vendors). Some of the vendors of beryllium, such as Beryllium Co., Beryllium Corp., and others, prefer the volumetric method because of its speed. The vendors report a coefficient of variation of about 0.5 percent for the titration, and the gravimetric method is capable of a coefficient of variation of 0.25 percent. Following a comparison of the two methods at Rocky Flats, it was concluded that fewer repeated determinations were required when the titration method was used. Coefficients of variation of 0.14 and 0.12 percent were calculated based upon duplicate volumetric determinations and triplicate gravimetric determinations, respectively, for each sample in the comparison. It was the consensus of opinion that the titration method is satisfactory as long as the beryllium samples assay greater than 98.5 percent, but a better method would be required if the beryllium content is lower. Present supplies assay between 98.4 and 98.5 percent.

... exist but are not with...
... In the...
... from a...
... are...
... in 99.0...
... results a coeff...
... of beryllium...
... is requir...
... and ignition to the...
... beryllium chloride, and separation...
... sodium phosphate which is either ignited and weighed or dissolved...
... phosphate titrated with standard bis... solution. None of these...
... methods is satisfactory.

Beryllium Oxide Determination

Oxygen is introduced into the beryllium pieces during machining and sintering operations, and metal entering the fabrication process with a low concentration of oxygen becomes oxidized to the extent of about one percent during processing. Therefore, the sampling problem especially with respect to the time the material is sampled, is critical. The vendors prefer to take samples of the turnings between the machining and the sintering operations, and discrepancies often occur when the vendor's results are compared with the analyses obtained following sintering.

As in the assay of beryllium, there are two methods which are prevalent for determining beryllium oxide in beryllium. In one method, the sample is reacted with hydrogen chloride gas at elevated temperature, and the beryllium metal is volatilized as the chloride leaving the beryllium oxide as a residue which is weighed. In the second method, bromine in anhydrous methanol is used to dissolve the beryllium metal leaving the beryllium oxide unattacked. The residue is dissolved in sulfuric acid, and the beryllium determined spectrophotometrically. The coefficient of variation in determining 1.5 percent beryllium oxide is about 5 percent.

The second method is faster and equipment requirements are less. Discrepancies frequently occur, as mentioned previously, between results obtained by the vendors and by the Rocky Flats Plant. It is believed that some of the discrepancies are caused by the presence of beryllium nitride which does not dissolve consistently in bromine-methanol. Errors caused by surface contamination are eliminated by cleaning the samples. Pickling in sodium bifluoride solution is effective for this purpose. Other errors are believed to be caused by the sampling. The seriousness of these discrepancies is most evident when the results for the beryllium and the beryllium oxide concentrations are added. The average values obtained for beryllium in five samples by four participating laboratories were 99.04, 98.66, 98.63, 98.47, and 98.55 percent. The corresponding concentrations of beryllium oxide were 1.28, 1.69, 1.83, 2.23, and 1.87 percent, giving totals of 100.32, 100.35, 100.46, 100.69, and 100.42 percent. The "safety factor" of 0.4 percent above the specification of 98.0 percent beryllium, as mentioned earlier, seems very inadequate, and complacency about the assay methods and the beryllium oxide determinations is not warranted.

... of the ...
... of the ...

... ..

... .. by methods. Concentration
... .. by

... .. in the concentration range of 2 to
determined by two methods (by the British). The sample is dissolved in
... .. and the chloride is precipitated as silver chloride which is
... .. and the determined spectrographically
... .. but the reproducibility
Alternatively, the chloride is separated by pyrohydrolysis, precipitated as
silver, and weighed. Carbon is usually determined by direct combustion
in which a 0.6 gram sample is mixed with 2 grams of carbon-free tin and carried in
1.5 liters of oxygen at 1000 to 1100°C. in a period of five minutes. The
sample reacts too rapidly, and dilution of the oxygen with inert gas to decrease
the reaction rate prevents complete reaction.

Although the spectrographic determination of impurities has been discussed in
some detail at previous conferences, especially by personnel from Livermore,
this subject was not discussed here.