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Note

## The Determination of Molybdenum, Uranium and Silicon in Molybdenum and Uranium Silicides

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In the course of an investigation of refractory silicides of molybdenum and uranium<sup>1</sup>, as well as multiphase systems containing molybdenum, uranium and silicon<sup>2</sup>, the problem of analytical determination of these elements in such systems has appeared. Methods hitherto recommended for the analytical determination of molybdenum, uranium and silicon in various materials<sup>3-6</sup> have been examined. However, none of these methods could be directly applied for the analysis of the samples of this kind.

The silicides tested were decomposed by (i) melting with sodium peroxide, (ii) dissolving with a mixture of hydrofluoric and sulphuric acid, and (iii) with a mixture of hydrofluoric and nitric acid, for the determination of silicon, uranium and molybdenum, respectively. The recommended method of the simultaneous determination from three separate weighings is simpler, quicker and more accurate than a progressive method by which the determination could be done on the same sample.

Silicon in the melt is determined gravimetrically as silica by dehydration with perchloric acid, as suggested by Willard and Cake<sup>3</sup> for the determination of silicon in steels. Molybdenum or uranium cannot be determined in the filtrate after the determination of silicon because of the presence of foreign ions<sup>7</sup>. Methods for the separation of molybdenum<sup>3</sup> or uranium<sup>3,6</sup> are lengthy, and quantitative separation of uranium is often impossible<sup>6</sup>.

Oxidation of molybdenum compounds yields molybdenum trioxide<sup>4</sup> as the final product. Consequently, the product of decomposition of molybdenum silicide with hydrofluoric and nitric acid, after volatilization of the silicon, can be converted to molybdenum trioxide by ignition in the air and weighed.

Silicon was removed from the uranium silicide sample by decomposition with a mixture of hydrofluoric and sulphuric acid. The residue could not be converted quantitatively to  $U_3O_8$  by ignition since the results obtained for uranium were low, probably due to the reaction described by Katz and Rabinowitch<sup>8</sup> and Ferris and Baird<sup>9</sup>. However, as the decomposition product of uranium silicides is soluble in sulphuric acid, it was converted to a form suitable for reduction with the Jones reductor, and then uranium determined in solution by titration with potassium permanganate<sup>3</sup>.

The analytical methods have been verified on standard samples and the relative standard error of the results amounts to 0.5% for all the elements.

## EXPERIMENTAL

*Determination of Molybdenum*

Molybdenum silicide (0.1 to 0.2 g) was gently warmed in a platinum crucible with concentrated nitric acid (6–8 ml) to which a few drops of concentrated hydrofluoric acid had been added. After the sample was dissolved, concentrated sulphuric acid (1–2 ml) was added and the solution evaporated to dryness. The dry residue of molybdenum trioxide was ignited for two hours (550–600°C) and weighed.

*Determination of Uranium*

A sample of uranium silicide (about 0.3 g), moistened in a platinum dish with diluted sulphuric acid (1:1) was decomposed by dropwise addition of concentrated hydrofluoric acid. Diluted sulphuric acid (2.5 ml) was added to the residue, which was then transferred by rinsing with distilled water to a 300-ml glass beaker. Concentrated sulphuric acid (8.5 ml) and hydrogen peroxide (30%) were added to the solution until it turned yellow. The solution was warmed until the decomposition of hydrogen peroxide was complete, diluted with distilled water, filtered, the filtrate transferred to a 200-ml volumetric flask and made up to the mark with distilled water.

For the determination of uranium, 10 ml of the solution was used, reduced in the Jones reductor and titrated with 0.02 N  $\text{KMnO}_4$ .

*Determination of Silicon*

A sample of silicide (0.3 g) mixed with ten times its volume of sodium peroxide was melted in an iron crucible for about 30 minutes. The melt was leached with diluted hydrochloric acid (1:1) and hot distilled water and transferred to a 400-ml glass beaker. If dissolution is incomplete, some diluted hydrochloric acid, followed by a few milliliters of concentrated nitric acid should be added. Concentrated perchloric acid (50–70 ml) was added to the solution and the contents of the beaker was then carefully evaporated on a hot plate until dense vapours of perchloric acid were evolved. After that, the solution was left standing on a hot plate for another 30 minutes and then cooled. To the solidified mass four times its volume of distilled water was added. Thus all perchlorates were dissolved while the precipitate of silicic acid remained. The precipitate was filtered off (filter paper »Whatman 544«) and thoroughly washed with hydrochloric acid (1:1) and water. The precipitate should be washed very carefully since the remaining perchlorates might cause minor explosions during the ignition. Very accurate results can be obtained if the filtrate is evaporated again and filtered.

The filter paper with the precipitate was transferred to a platinum crucible, dried, ignited for 30 minutes at 1100°C and weighed. The precipitate, moistened with diluted sulphuric acid (1:1), was dissolved in hydrofluoric acid (1–2 ml). After evaporation and subsequent ignition for 30 minutes at 1100°C the silicon content was determined from the difference in weight of the crucible.

*Chemicals*

All chemicals used were analytical grade reagents: »Analar« from Hopkin and Williams Ltd. or »pro analysi« from Merck-Darmstadt. The samples were obtained by melting spectroscopically pure components (Johnson, Matthey and Co., Ltd.) without container by a floating zone method described by Ban and Sikirica<sup>1,2</sup> and identified as intermetallic phases for the first time by these authors.

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## IZVOD

## Određivanje molibdena, urana i silicija u silicidima molibdena i urana

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Opisana je metoda za pripremu uzoraka pri određivanju molibdena, urana i silicija u odgovarajućim silicidima. Metoda se sastoji od (1) razaranja silicida taljenjem s natrijevim peroksidom, (2) otapanja u smjesi fluorovodične i sumporne kiseline i (3), ako je potrebno, otapanja u smjesi fluorovodične i dušične kiseline. Nakon otapanja u pojedinačnim uzorcima određuju se silicij i molibden gravimetrijski (kao  $\text{SiO}_2$ , odnosno  $\text{MoO}_3$ ), a uran se nakon redukcije u Jonesovu reduktoru određuje volumetrijski pomoću permanganata. Relativna standardna pogreška određivanja iznosi 0,5%.

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