The Separation of Selenium(IV) and Selenium(VI) by Solvent Extraction

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As a method for the mutual separation of selenium(IV) and selenium(VI), precipitation with sulfur dioxide gas[1] has been used. The present author has now tried to separate them by extraction with TBP (tributyl phosphate) and Na(DDTC) (sodium diethyldithio carbamate). As a result, a more rapid and simple method will be elaborated.

Selenium(IV) forms a yellow compound in hydrochloric acid media with DDTC, this chelate can be extracted by TBP from a 0.05 N—0.1 N hydrochloric acid solution quantitatively, while selenium(VI) does not form DDTC complexes under these conditions. The author has devised the following separation prosedure based on the above properties.

Experimental and Results

The Preparation of the Radioactive Selenium(IV) Solution and the Radioactive Selenium(VI) Solution.—^{75}Se was added to a nitric acid solution (1 : 1) of standard selenium(IV) solution. The solution was then evaporated, dried up, and dissolved with a 0.1 N hydrochloric acid solution. One milliliter of this solution contained 100 μg. of Se*(IV). The radioactive selenium(VI) solution was prepared using radioactive selenium(IV) by the method of Dennis and Koller.[2]

The Determination of the Distribution Ratios.—The distribution ratios of selenium(IV) and selenium(VI) in the DDTC-HCl-TBP system were studied. The radioactive selenium(IV) solution (or the radioactive selenium(VI) solution) and 0.1 M Na(DDTC) were mixed with 5 ml. of hydrochloric acid in various concentrations and then shaken with an equal volume of TBP(pre-equilibrated with each hydrochloric acid solution). The equilibrium was established within 1 min. The two phases were then separated by centrifuging, and a 1 ml. portion was taken from each phase. The γ-radioactivity was measured with a well-type scintillation counter. The data obtained are shown in Fig. 1, where D is the distribution ratio. It is clear from this figure that the mutual separation of selenium(IV) and selenium(VI) is possible at the acidity of a hydrochloric acid solution of 0.05—0.1 N.

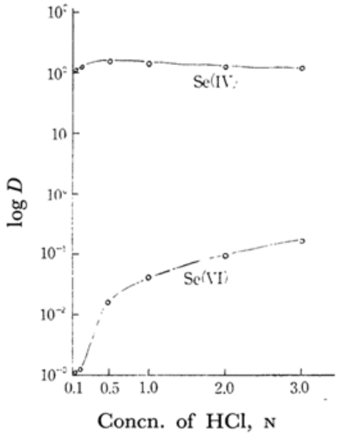

Fig. 1. Distribution of selenium in DDTC-HCl-TBP system.

The effects of the ratio of DDTC to selenium were next investigated. The smallest DDTC-to-selenium ratio, giving the highest extraction, was between 4 and 5 to 1 on a molar basis.

The Back-Extraction of Selenium(IV).—Selenium(IV) in the TBP phase is back-extracted by shaking for one minute with 20 ml. of a 10% perchloric acid solution and 1 ml. of a hydrogen peroxide solution. More than 99% of the selenium(IV) was recovered in the aqueous phase by two back extractions.

The Mutual Separation of Selenium(IV) and Selenium(V).—A radioactive (or inactive) selenium(IV) solution and an inactive (or radioactive) selenium(VI) solution were mixed (selenium(IV): 10 mg., selenium(VI): 10 mg.). The solution was then adjusted to the acidity of a 0.05—0.1 N hydrochloric acid solution. The total volume was 20 ml. After the addition of 2 ml. of a 10% Na(DDTC) solution, the solution was shaken with 5 ml. of TBP in a separating funnel for one minute. The extraction was then repeated two times. After the selenium(IV) has been extracted with TBP, leaving selenium(VI) in the aqueous phase, the selenium(IV) was back-extracted twice as above. Then the aqueous phase was separated. The γ-activity of the aqueous and organic phases was measured with a well-type scintillation counter. By this simple procedure, these ions can be separated quantitatively.

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1) H. Bode and H. D. Stemmer, *Z. Anal. Chem.*, **155**, 96 (1957).

2) L. M. Dennis and J. P. Koller, *J. Am. Chem. Soc.*, **41**, 949 (1919).