

Short Communication

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A NEW METHOD FOR THE CONVERSION OF U(VI) TO U(IV)

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A new method for the conversion of U(VI) solutions to U(IV) solutions has been developed. The method presented can be preferred over the conventional electrolytic reduction methods¹⁻³ or zinc amalgam reduction method⁴ due to number of advantages.

Experimental

The catalytic hydrogenation method for the reduction of uranyl solutions is briefly described below.

- (1) Catalyst used: Between 0.1 - 0.2 g of 200 platinized alumina.
- (2) Concentration of the uranyl (acetate, nitrate, perchlorate, sulphate) solutions: $(10^{-3} - 10^{-1})$ molar
- (3) Volume of the solution being reduced: 1 ml - 100 ml.
- (4) Rate of flow of the hydrogen gas: 100 cc - 500 cc per min.
- (5) Time for the completion of the reduction, i.e. when the yellow colour of the uranyl ion completely fades and dark green uranous colour is marked: 20-35 min.
- (6) Cu^{2+} ions should be absent and the catalyst should be washed with water after every operation.
- (7) In a typical run 60 ml of 0.1 molar solution of uranyl perchlorate standardized by the method of Kolthoff and Sandell⁵ was taken and hydrogen was passed at a rate of 500 cc per min for a period of 25 minutes. The corresponding U(IV) was analysed for its U(IV) content by titrating aliquots of the solution against standard $\text{K}_2\text{Cr}_2\text{O}_7$ and ceric sulphate solutions⁶⁻⁷. The conversion from U(VI) to U(IV) was found to be complete and the moles of oxidizing agents consumed in these titrations corresponded to two electron conversion stoichiometry which rules out any possibility of the presence of U(III). The U(IV) solutions were scanned for UV/visible spectrum on a SP 800 Pye Unicam spectrophotometer, at various intervals of time. The resulting curves are shown in the Fig. 1.

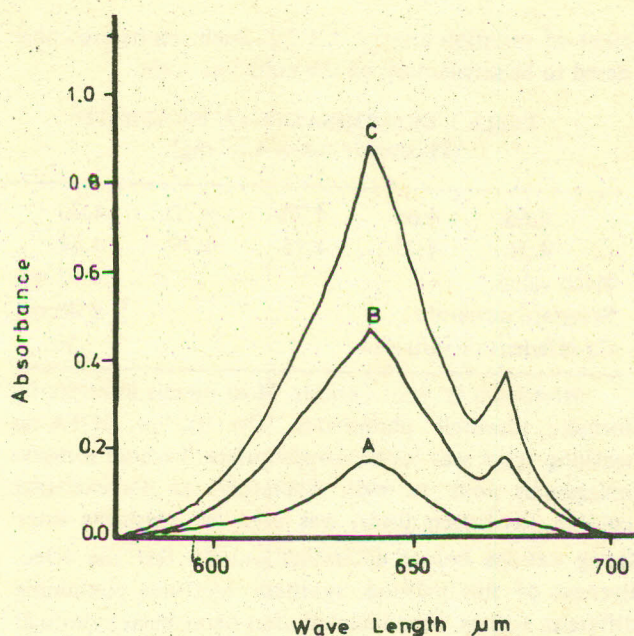


Fig. 1. Spectra of diluted U(IV) samples from a 0.1 M hydrogenated uranyl perchlorate solution: Maximum U(IV) concentration = $1.5 \times 10^{-3}\text{M}$; Curve A taken after 4 min., Curve B taken after 10 min., Curve C taken after 25 min. of hydrogenation.

- (8) Hydrogen flow rate of 100 cc to 500 cc per min. was maintained in various experiments in an open vessel. Since U(VI) to U(IV) conversion is two electron transfer the following equation should hold:



The excess hydrogen escapes from the open vessel and partial pressures could not be measured as the system was not closed. Hence, the moles of hydrogen absorbed can not be observed.

- (9) The catalyst platinized alumina is insoluble in aqueous solution and it can be removed later either by filtration through sintered glass or by centrifuging the hydrogenated sample.
- (10) The process is specially feasible for small volumes which are sometimes essentially required as one has to work in small volumes due to expected radiation hazards from a radioactive isotope like U^{235} .

Discussion

Electrolytic reduction method of converting u (vi) to u (iv) has long been preferred over any other methods. But this technique has got the following drawbacks.

- (a) Small volumes of the uranyl solutions are difficult to reduce.
- (b) Nitrate ions are to be removed before the reduction otherwise analysis is difficult.
- (c) Over reduction U^{3+} ions.
- (d) Uranyl solutions prepared in the 0.5M

acid concentration, cannot be reduced.

The method presented can be preferred over the previously employed methods as U(VI) solutions of low concentrations even in small volumes can be reduced by this method. Nitrate ion do not interfere in the reduction process and also U^{3+} ions are not produced. All of the reported methods require atleast 0.5M or more acid concentration for the reduction process while in this technique even less than 0.05M acid concentration has been found to produce 100% conversion to U(IV). Lastly the method presented is easy, inexpensive and can be adopted even in smaller laboratories.

References

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