

## Precipitation of uranium quinolin-8-olate from homogeneous solution by urea hydrolysis

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**Abstract.** A very crystalline precipitate of uranium quinolin-8-olate (uranyl oxinate) has been obtained from homogeneous solution by utilising urea hydrolysis to raise the pH of the initially acid solution of uranium (VI) in the presence of sodium acetate and the precipitant. The precipitate so obtained is stoichiometric unlike the one obtained in conventional precipitation and possesses the same composition (uranium : oxine ratio) irrespective of the pH of the final solution unlike that obtained in earlier PFHS methods. The results obtained show that the determination is not affected by the presence of other metal ions when the precipitation is carried out in the presence of EDTA and the precipitate obtained by PFHS is also more thermally stable.

**Keywords.** Uranium(VI) complex ; quinolin-8-ol ; precipitation from homogeneous solutions ; urea hydrolysis ; thermal analysis.

### 1. Introduction

Precipitation from homogeneous solution (PFHS) technique is often employed to produce pure and crystalline precipitates and the precipitates so obtained also possess a better stoichiometry when compared to the precipitates obtained by the conventional method (Gordon *et al* 1959 ; Cartwright *et al* 1967). For example, copper cupferrate obtained by PFHS method can be weighed directly for the gravimetric determination of the metal (Heyn and Dave 1960) whereas the same obtained by the conventional method is to be ignited to oxide before weighing. Corsini and Abraham (1968) reported that the uranium quinolin-8-olate (uranyl oxinate) obtained by direct addition of the reagent was deficient in oxine. This red compound  $\text{UO}_2(\text{C}_9\text{H}_6\text{ON})_2 \cdot \text{C}_9\text{H}_7\text{ON}$ , which is usually employed for the analysis of uranium (VI) solutions was mentioned several times in literature (Hecht and Reich-Rohrwig 1929 ; Frere 1933 ; Fleck 1937 ; Classen and Visser 1946 ; Moeller and Wilkins 1953 ; Wendlandt 1956 ; Van Tassel and Wendlandt 1959, 1961 ; Bullwinkel and Nobel 1959 ; Horton and Wendlandt 1963 ; Tackett 1964 ;

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Majee and Gordon 1965; Majee and Woodward 1966; Fleming and Lynton 1967; Milner *et al* 1960), but the deficiency of oxine was not observed. Similarly, the workers who studied the PFHS determination of uranium quinolin-8-olate by the hydrolysis of 8-acetoxyquinoline (Bordner *et al* 1961) and also by evaporation of mixed solvents (Howick and Rihs 1964) were not aware of this problem as Corsini and Abraham's (*loc. cit.*) work was published much later. On the other hand it was reported that the complex obtained by PFHS method had different compositions depending on the pH of the solution, a dark red compound  $\text{UO}_2(\text{C}_9\text{H}_6\text{ON})_2 \cdot \text{C}_9\text{H}_7\text{ON}$  was obtained at pH 5.0 and an orange compound  $(\text{UO}_2(\text{C}_9\text{H}_6\text{ON})_2)_2 \cdot \text{C}_9\text{H}_7\text{ON}$  resulted when the pH was increased to 6.8 (Bordner *et al* 1961). Hence the earlier observation of deficiency of oxine in the red compound may be due to the coprecipitation of the latter compound with the former.

Since PFHS methods produced stoichiometric precipitates which could be weighed directly unlike in conventional methods (Cartwright *et al* 1967; Siva Reddy and Krishna Reddy 1980) in the present investigation, uranium quinolin-8-olate has been precipitated from homogeneous solution by urea hydrolysis so as to remove the deficiency of oxine. Crystal sizes and thermal behaviour of the precipitates obtained by PFHS and conventional methods are compared.

## 2. Experimental

### 2.1. Reagents

All the chemicals used were of AnalaR grade, supplied by BDH. Uranium (VI) solution: About 8.5 gm of uranyl nitrate,  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was transferred to a 1-litre flask, dissolved in water and diluted to the mark. The solution was standardised gravimetrically using diammonium uranate procedure (Vogel 1975). Quinolin-8-ol (oxine) solution: 2% solution (w/v) in acetone.

Dilute nitric acid: Aqueous solution, 1:1 (v/v) of  $\text{HNO}_3$ .

Dilute ammonia solution: Ammonium hydroxide solution, 1:1 (v/v).

### 2.2. Apparatus

Elico pH-meter model LI-10 was used in the investigation. The sensitivity of the instrument is 0.05 pH units. The particle sizes were measured using Leitz-Wetzler microscope and photomicrographs were also taken using the same microscope fitted with camera. The thermograms were recorded using a thermobalance supplied by Stanton Redcroft. The crucible used was made of alumina and the thermocouple employed was constructed from platinum and rhodium. The temperature was raised at the rate of 6° C/min. The samples were dried under vacuum for several days before recording the thermograms.

### 2.3. Procedure

An aliquot containing uranium (VI) was transferred into a clean 250 ml beaker and to it were added 10 gm of sodium acetate and 15 gm of urea. The initial pH of the solution was adjusted to 2.0 with 1:1 nitric acid. Quinolin-8-ol solution was added in excess and the contents were diluted to 150 ml. An indented glass rod was kept in the solution to avoid bumping and the beaker was covered with

a watch glass. The beaker was kept in a hot air oven maintained at 90° C for about 5 hr. The solution was cooled to room temperature and the precipitate was filtered through a weighed sintered glass crucible of medium porosity, washed with warm water (ca. temperature 40° C) and dried for 1 hr at 115–120° C and weighed.

### 3. Results and discussions

#### 3.1. Determination of uranium

Determination of uranium in the range 20–300 mg was successful and the results are presented in table 2. For a set of ten measurements of 81.25 mg of uranium (VI), the average amount and standard deviation were found to be 81.23 and 0.07 mg. For the same amount of uranium (VI), the amount found by bromometric procedure was 81.22 mg with a standard deviation of 0.12 mg. The microanalysis of the precipitate indicated the composition which correspond to  $\text{UO}_2(\text{C}_9\text{H}_6\text{ON})_2 \cdot \text{C}_9\text{H}_7\text{ON}$  (table 1).

Table 1. Microanalysis of the complex.

Element	Theoretical percentage	Percentage obtained
C	46.03	45.95
H	2.72	2.68
N	5.97	5.97

Table 2. Determination of uranium.

Amount of uranium taken* mg	Amount of uranium found, mg ( $n = 3$ )	Difference mg ( $n = 3$ )
8.1 <sub>8</sub>	8.1 <sub>6</sub>	0.0 <sub>8</sub>
20.3 <sub>1</sub>	20.3 <sub>2</sub>	0.0 <sub>1</sub>
40.6 <sub>2</sub>	40.5 <sub>8</sub>	0.0 <sub>4</sub>
60.9 <sub>3</sub>	60.9 <sub>0</sub>	0.0 <sub>3</sub>
81.2 <sub>3</sub>	81.2 <sub>3</sub>	0.0 <sub>7</sub> **
243.8	243.3	0.5
325.0	324.2	0.8

\* Based on gravimetric (ammonium diuranate) procedure.

\*\* Standard deviation for ten measurements.

The results show that the complex is not deficient in quinolin-8-ol. Even if the pH is increased beyond 9.0, it was observed that only dark red compound formed unlike in the earlier PFHS and conventional methods (Corsini and Abraham 1968 ; Bordner *et al* 1961 ; Howick and Rihs 1964). Moreover the complex possesses a good stoichiometry (no deficiency of oxine is observed). Addition of 2 to 3 fold excess of reagent did not affect the determination, though a slight excess ensured complete precipitation.

### 3.2. Particle size

The precipitate obtained is very dense and crystalline and higher amounts of uranium could be handled very easily. The distributions of particle sizes are given in table 3. The median value was obtained from the plots of particle size *vs.* logarithm of cumulative number. The median value calculated was  $192 \times 112 \mu$ . The precipitate obtained by conventional method is amorphous. The photomicrographs of the precipitate obtained are shown in figure 1.

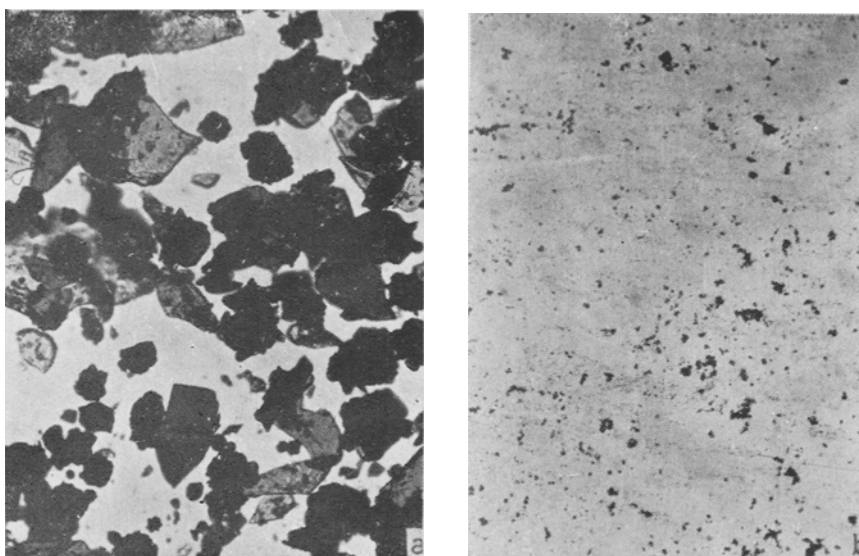
### 3.3. Thermal behaviour

The thermograms are shown in figure 2. The precipitate obtained from homogeneous solution did not lose weight up to  $200^\circ \text{C}$  whereas the same obtained by conventional method was stable up to  $180^\circ \text{C}$ . The precipitate yielded unsolvated chelate on further heating due to the sublimation of supplementary quinolin-8-ol molecule and the *bis*-complex,  $\text{UO}_2(\text{C}_9\text{H}_6\text{ON})_2$  was stable in the range of  $240$ - $310^\circ \text{C}$ . At  $440^\circ \text{C}$ , the weight of the precipitate corresponded to  $\text{U}_3\text{O}_8$  and from this temperature no weight loss was recorded. For the precipitate obtained by conventional method, the formation of *bis*-complex and oxide were observed at  $220^\circ \text{C}$  and  $420^\circ \text{C}$  respectively. The thermograms recorded in the present procedure agreed fairly well with the earlier ones but not with the pyrolysis curve recorded by Duval (1953) who stated that formation of  $\text{U}_3\text{O}_8$  did not take place before  $940^\circ \text{C}$ .

Table 3. Distribution of particle sizes of the precipitate obtained by PFHS.

Total number of particles counted = 500  
1 microscopic division =  $16 \mu$ .

Lengthwise distribution		Breadthwise distribution	
Microscopic divisions	Percentage of distribution	Microscopic divisions	Percentage of distribution
1-10	64.7	1-4	52.6
11-20	16.8	5-8	18
21-30	11	9-12	15
31-40	5	13-16	6.6
41-50	2	17-20	5
51-60	0.5	21-24	2.8



**Figure 1.** Photomicrographs of uranium quinolin-8-olate (a) from homogeneous solution, (b) by conventional method.

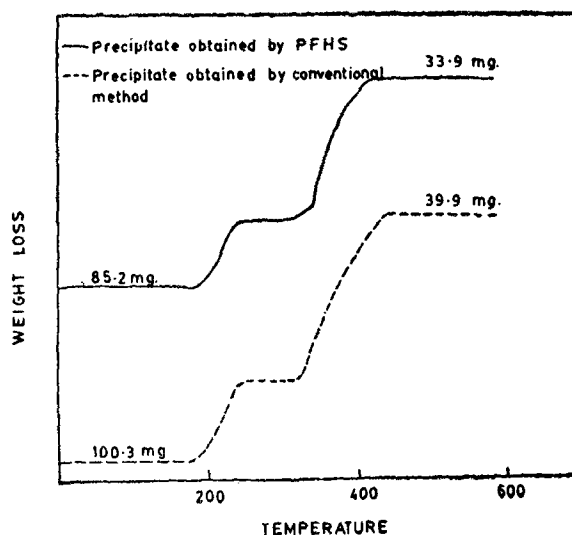


Figure 2. Pyrolysis of uranium quinolin-8-olate.

### 3.4. pH increase in presence of various anions

The function of the anion in urea hydrolysis is three fold ; (i) buffer action, (ii) complex formation and (iii) incorporation of anion in the precipitate and formation of basic salt. In the precipitation of hydroxides and basic salts, the anions help in the formation of basic salts though other reasons are not ruled out (Cartwright 1967). Similarly in the precipitation of neutral salts or complexes, the anion serves mainly as buffer, though complex formation is not ruled out (Siva Reddy and Krishna Reddy 1979). This can be understood only from the plots of pH increase with time and percentage recovery of the metal with pH in presence of various anions. pH increase in the presence of various anions is shown in figure 3 and the percentage recovery of uranium (VI) with pH is given in figure 4. pH increase is very rapid in the presence of ammonium chloride, ammonium sulphate, tartaric acid and succinic acid and slow in the presence of acetate and formate buffers. A very crystalline precipitate is obtained in the presence of sodium acetate and ammonium acetate. The pH increase with time shown in figure 3 is for nearly 80 mg of uranium (VI), 15 ml of quinolin-8-ol solution and 10 gm of buffer. Each value represented in the figure is the average for six experiments. From the plot of percentage recovery of uranium with pH (figure 4), it is seen that the initial precipitation process is delayed in the presence of succinic acid and EDTA due to complex formation other buffers appear to control pH raise only.

### 3.5. Effect of diverse ions

When precipitation was carried out in the presence of EDTA, 100 mg each of copper (II), iron (III), zinc (II), cadmium (II), lead (II), aluminium (III) and thorium (IV) did not interfere in the determination of 81.25 mg of uranium. The results are presented in table 4.

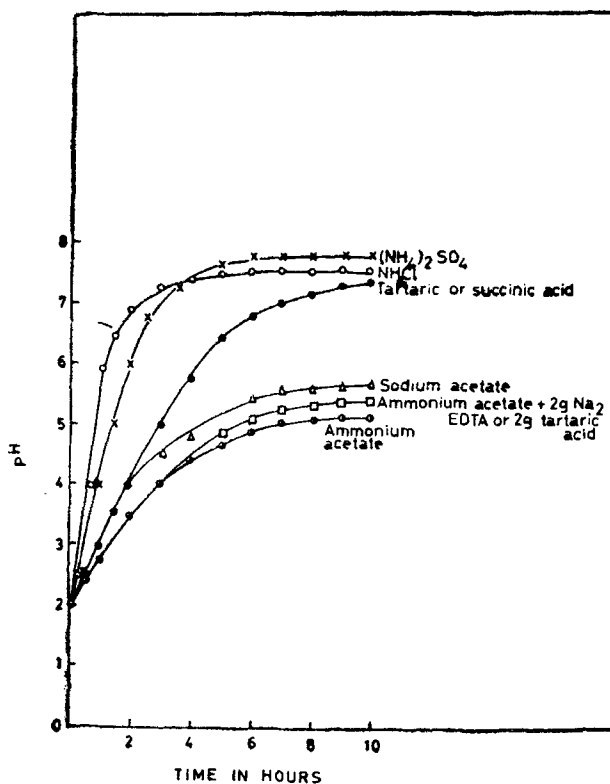


Figure 3. pH increase with time in presence of various buffers.

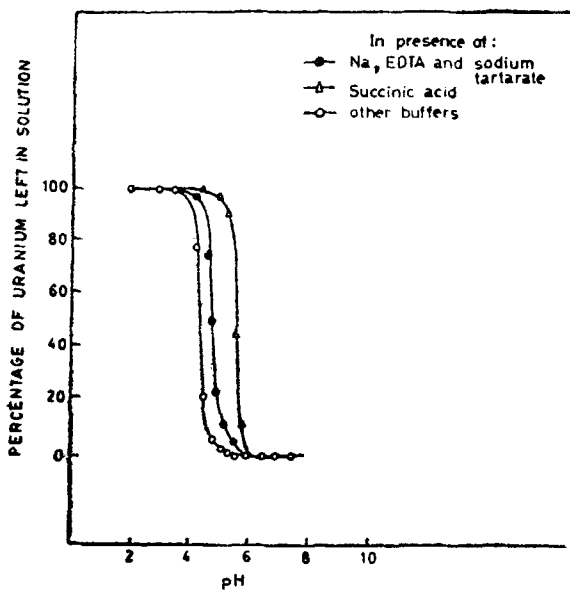


Figure 4. Percentage of uranium left in solution with pH

Table 4. Effect of cations.

Initial molarity of EDTA in the solution = 0.04 M  
 Amount of cation added = 100 mg.

Cation added	Amount of uranium found for 81.2 mg of uranium taken mg	Difference mg
Copper(II)	81.2 <sub>0</sub>	0.0 <sub>5</sub>
Nickel(II)	81.1 <sub>8</sub>	0.0 <sub>7</sub>
Iron(III)	81.3 <sub>2</sub>	0.0 <sub>7</sub>
Manganese(II)	81.2 <sub>0</sub>	0.0 <sub>5</sub>
Zinc(II)	81.2 <sub>0</sub>	0.0 <sub>5</sub>
Cadmium(II)	81.1 <sub>8</sub>	0.0 <sub>7</sub>
Lead(II)*	81.3 <sub>4</sub>	0.0 <sub>9</sub>
Aluminium(III)	81.3 <sub>2</sub>	0.0 <sub>7</sub>
Thorium(IV)*	81.2 <sub>8</sub>	0.0 <sub>7</sub>

\* Added in the form of nitrates.  
 Other salts are added in the form of sulphates.

#### 4. Conclusion

From the above discussion, it is clear that the PFHS determination of uranium by urea hydrolysis is accurate. No deficiency of quinolin-8-ol (oxine) or differences in compositions has been observed unlike in earlier conventional and PFHS methods. The highly crystalline precipitate obtained in the present method facilitated easy filtration and less interference from impurities.

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#### References

- Bordner J, Salesin E D and Gordon L 1961 *Talanta* **8** 579  
 Bullwinkel E P and Nobel Jr P 1959 *J. Am. Chem. Soc.* **81** 813  
 Cartwright P F S 1967 *Talanta* **14** 690  
 Cartwright P F S, Newman E J and Wilson B W 1967 *Analyst* **92** 664  
 Classen A and Visser J 1946 *Rec. Trav. Chim.* **65** 211



- Corsini A and Abraham J 1968 *Talanta* **15** 562
- Duval C 1953 *Inorganic thermogravimetric analysis* (Amsterdam : Elsevier) 510
- Fleck H R 1937 *Analyst* **62** 378
- Fleming J E and Lynton W 1967 *Can. J. Chem.* **45** 1637
- Frere F J 1933 *J. Am. Chem. Soc.* **55** 4362
- Gordon L, Salutsky M L and Willard H H 1959 *Precipitation from homogeneous solution* (New York : John Wiley) 2.
- Hecht F and Reich-Rohrwig W 1929 *Monatsh. Chem.* **53-54** 596
- Heyn A H A and Dave N G 1960 *Talanta* **5** 119
- Horton G R and Wendlandt W W 1963 *J. Inorg. Nucl. Chem.* **25** 247
- Howick L C and Rihs T 1964 *Talanta* **11** 667
- Majee R J and Gordon L 1965 *Talanta* **12**, 441, 445
- Majee R J and Woodward I 1966 *Talanta* **13** 209
- Milner G W C in Wilson C L and Wilson D W 1960 *Comprehensive analytical chemistry*, Vol. 1C (Amsterdam : Elsevier) 610
- Moeller T and Wilkins D H 1953 *Inorganic synthesis* **4** (New York : McGraw-Hill) 101
- Siva Reddy G and Krishna Reddy Y 1979 *Talanta* **26** 245
- Idem 1980 *Analyst* **105** 391
- Tackett J E and Sawyer D J 1964 *Inorg. Chem.* **3** 692
- Van Tassel J H and Wendlandt W W 1959 *J. Am. Chem. Soc.* **81** 813
- Van Tassel J H and Wendlandt W W 1961 *J. Am. Chem. Soc.* **83** 810
- Vogel A I 1975 *A text-book of quantitative inorganic analysis* (London: ELBS and Longmans p. 539
- Wendlandt W W 1956 *Anal. Chem.* **28** 499