

# Study of the dehydration process of uranyl difluoride hydrates stable under usual conditions of temperature, pressure and atmospheric moisture

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## Abstract

The dehydration of the uranyl difluoride hydrate stable under usual conditions of temperature, pressure and atmospheric moisture has been investigated by controlled transformation rate thermal analysis, controlled thermogravimetry and by variable temperature X-ray diffraction under controlled atmosphere. The importance of the residual water vapor above the sample has been demonstrated. It was possible to distinguish three steps in the dehydration of uranyl difluoride hydrate. These steps are: the dehydration of the solid solution usually named  $\beta$ , the transformation of  $\beta$  to the usually named  $\alpha$ , and the loss of water from phase  $\alpha$ . The range of existence of the two solid solutions  $\alpha$  and  $\beta$  have been defined. © 1998 Elsevier Science S.A. All rights reserved.

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## 1. Introduction

The aim of the present work was to accurately characterise the range of existence of the uranyl fluoride hydrate stable under usual conditions of temperature, pressure and atmospheric moisture and to determine the number of steps occurring in the course of the synthesis of an anhydrous compound from the stable hydrate.

The first step in the fabrication of nuclear fuel is the conversion of enriched uranium hexafluoride to uranium dioxide powder. The 'dry conversion process' is currently a preferred route for the preparation of  $\text{UO}_2$ . In this technology, difluoro dioxo uranium VI, often termed uranyl difluoride, is an important intermediate, and its reduction to  $\text{UO}_2$  determines the mechanical and chemical qualities of the final ceramic powder.

The structure of  $\text{UO}_2\text{F}_2$  was first determined, by Zachariassen [1], and neutron powder diffraction studies were subsequently carried out by Atoji and Mc Dermott [2] and Taylor and Wilson [3].  $\text{UO}_2\text{F}_2$  has a layer structure; planes of uranium atoms are 5.22 Å apart and the axis of the uranyl group is normal to these planes. This structure allows the insertion of water molecules between the layers and a number of uranyl difluoride hydrates are known.

However, crystallographic results [4–16] are ambiguous and contradictory. Some authors [10–12] have reported stoichiometric hydrates,  $\text{UO}_2\text{F}_2 \cdot 4\text{H}_2\text{O}$  and  $\text{UO}_2\text{F}_2 \cdot 3\text{H}_2\text{O}$ , as well as solid solutions, that based on the dihydrate is termed  $\gamma$ . Its range of composition can vary between  $\text{UO}_2\text{F}_2 \cdot 1.6\text{H}_2\text{O}$  and  $\text{UO}_2\text{F}_2 \cdot 2.5\text{H}_2\text{O}$  and the phase of composition limits  $\text{UO}_2\text{F}_2 \cdot 0.8\text{H}_2\text{O}$  and  $\text{UO}_2\text{F}_2 \cdot 1.4\text{H}_2\text{O}$  is termed  $\beta$ . Moreover, anhydrous uranyl difluoride can accept up to 0.6 mole of water per mole of  $\text{UO}_2\text{F}_2$ . This solid solution is named  $\alpha$ .

However, other studies of the system  $\text{UO}_2\text{—H}_2\text{O—HF}$  show that the highest hydrate of uranyl difluoride is  $\text{UO}_2\text{F}_2 \cdot 2\text{H}_2\text{O}$  [6,7]. Some of these studies specify three crystalline modifications for the dihydrate, others mention two different crystalline forms for  $\text{UO}_2\text{F}_2 \cdot 1.5\text{H}_2\text{O}$  [7,14–16]. Yet others [14] indicate that the stable form in air has neither the same composition nor the same X-ray diffraction pattern as that found by the isopiestic method [7].

## 2. Experimental

### 2.1. Sample

The sample of uranyl difluoride hydrate was obtained by leaving the anhydrous product in ambient air, at 20°C, for 5

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days. The composition of the sample, established by thermogravimetric analysis, is ca.  $\text{UO}_2\text{F}_2 \cdot 1.5\text{H}_2\text{O}$ .

## 2.2. Apparatus

The dehydration of uranyl difluoride has been investigated by controlled transformation rate thermal analysis (C.R.T.A.) [17]. The principle of this method is to maintain the speed of the reaction at a desired value acting on sample temperature. Two specific apparatus following this principle have been built. The first (Fig. 1) works under reduced pressure [18] and pumping assures the continuous evacuation of water vapor resulting from dehydration reaction. The study of reactions under constant atmospheric pressure of any gas is made possible using another apparatus (Fig. 2). In each case, the speed of the reaction and the local water vapor pressure are maintained constant throughout the reaction.

The dehydration reaction has also been studied by controlled thermogravimetry. This was made possible with the aid of a specific apparatus, the principle of functioning of which is described in Fig. 3. In this case, heating of the sample is possible only if the weight of the sample is constant. This method allows better separation of the different steps of the reaction in comparison with traditional thermogravimetric analysis.

X-ray diffraction under controlled atmosphere and as a function of temperature was carried out using a device developed in this laboratory [19].

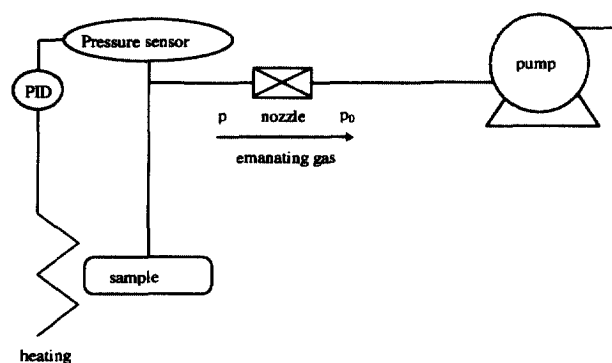


Fig. 1. Principle of C.R.T.A. apparatus functioning 'under vacuum'.

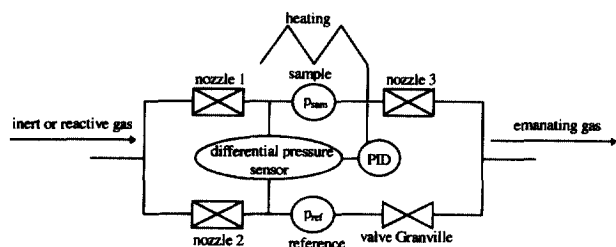


Fig. 2. Principle of C.R.T.A. apparatus functioning under atmospheric pressure.

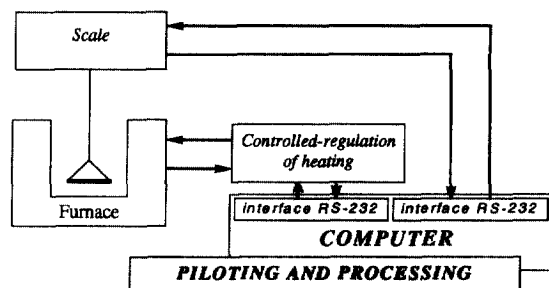


Fig. 3. Principle of apparatus for thermogravimetric analysis.

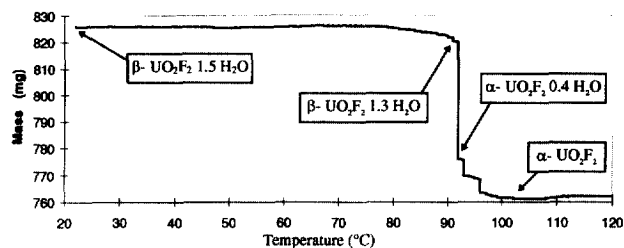


Fig. 4. Thermogravimetric analysis carried out in ambient air.

## 3. Results and discussion

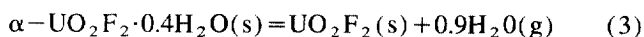
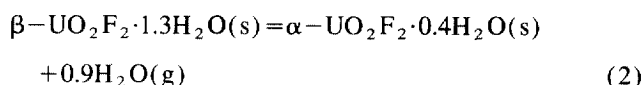
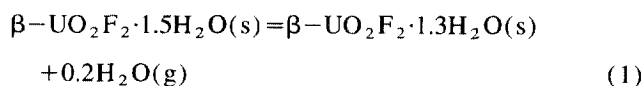
### 3.1. Thermogravimetric analysis

Thermogravimetric analysis was carried out in ambient atmosphere under which conditions values of hygrometry can vary between 40 and 80%, i.e., between ca. 6.6 and 13.2 mbar at 25°C.

Many regions are seen on the thermogram shown on Fig. 4. The initial composition of the hydrate is  $\text{UO}_2\text{F}_2 \cdot 1.5\text{H}_2\text{O}$ . The comparison of the X-ray diffraction pattern of this phase with those established by several authors [10,12] enable us to identify this sample as being the phase  $\beta$ . The composition of the hydrate  $\beta$  remains unchanged up to 78°C. From this temperature to 92°C a small loss of weight occurs which can be attributed to a change of composition of the solid solution  $\beta$  with the increase in temperature.

At 92°C, important weight loss imposes, in the particular experimental conditions of the 'controlled thermogravimetry', thermal invariance until the composition  $\text{UO}_2\text{F}_2 \cdot 0.4\text{H}_2\text{O}$ . For this composition, the host structure for the water molecules is no longer the hydrate  $\beta$  but that of anhydrous uranyl difluoride. It can accept water molecules into its structure without significant structural modification. This phase is named  $\alpha\text{-UO}_2\text{F}_2$ .

For the range of temperature studied, the following dehydration reactions can be written:



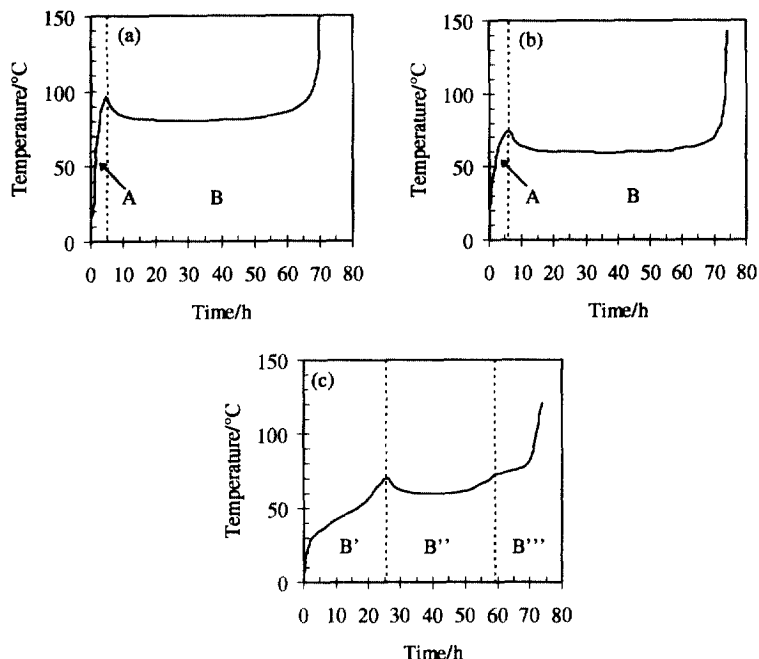


Fig. 5. (a and b) C.R.T.A. curves of the dehydration of  $\text{UO}_2\text{F}_2 \cdot 1.5\text{H}_2\text{O}$  carried out under 4 mbar water vapor pressure. (a) Under atmospheric pressure, (b) under vacuum. (c) C.R.T.A. curve of the dehydration of  $\text{UO}_2\text{F}_2 \cdot 1.5\text{H}_2\text{O}$  carried out under  $10^{-2}$  mbar water vapor residual pressure.

This study of the dehydration of the uranyl difluoride hydrate stable under normal conditions of temperature, pressure and hygrometry does not show the existence of any intermediate compounds between  $\beta$  and  $\alpha$ .

### 3.2. C.R.T.A.

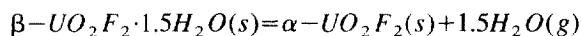
Dehydration is carried out under atmospheric pressure of nitrogen or 'under vacuum'. The partial pressure of water vapor (in the first case) or residual pressure of water vapor (in the second case) are measured and are kept constant. Fig. 5a and b represent C.R.T.A. curves obtained using a similar rate and under water vapor pressure of 4 mbar. The first experiment was performed under atmospheric pressure of nitrogen and the second 'under vacuum'. The third figure (Fig. 5c) corresponds to an experiment carried out 'under vacuum' with a residual pressure of  $10^{-2}$  mbar.

From the two first C.R.T.A. curves, two successive steps indicated by the letters A and B are observed. As the degree of advancement varies in C.R.T.A. linearly with time ( $d\alpha/dt = \text{constant}$ ), the short duration of the first step indicates little loss of weight. The second step is related to the transformation of  $\text{UO}_2\text{F}_2 \cdot 1.5\text{H}_2\text{O}$  to the anhydrous compound ( $\alpha\text{-UO}_2\text{F}_2$ ). This change occurs at about  $90^\circ\text{C}$  under atmospheric pressure and at  $60^\circ\text{C}$  under 4 mbar of residual water vapor pressure. The third experiment carried out under residual pressure of  $10^{-2}$  mbar allows, instead of one region B, three different regions ( $B'$ ,  $B''$  and  $B'''$ ) to be distinguished. Samples taken at different degrees of progress of the reaction in range  $B'$ , and analysed by X-ray diffraction reveal the presence of phase  $\beta$  only.

In the region  $B''$ , two phases can be detected:  $\alpha$  and  $\beta$ . X-ray diffraction in the range  $B'''$  shows lines characteristic only of the anhydrous compound.

The reactions related to the three dehydration steps  $B'$ ,  $B''$  and  $B'''$ , i.e., the steps occurring under low water vapor pressure, appear the same as those mentioned above (Eqs. (1)–(3)).

However, under water vapor pressure greater than  $10^{-2}$  mbar, only one dehydration step is seen. Thus 'under vacuum' or under atmospheric pressure:



These results confirm the influence of water vapor pressure on the thermal dehydration of uranyl difluoride hydrate. This is illustrated in Fig. 6, where three different C.R.T.A. curves obtained under three different water vapor pressures, are represented.

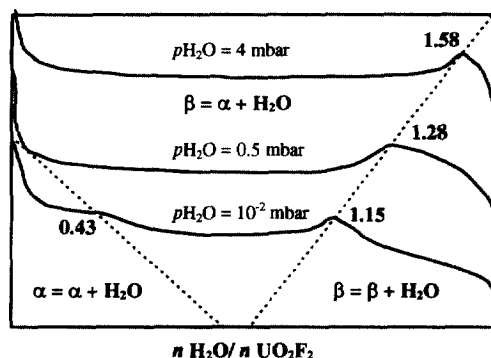


Fig. 6. Hydrates observed during dehydration of  $\text{UO}_2\text{F}_2 \cdot 1.5\text{H}_2\text{O}$  under different water vapor pressure.

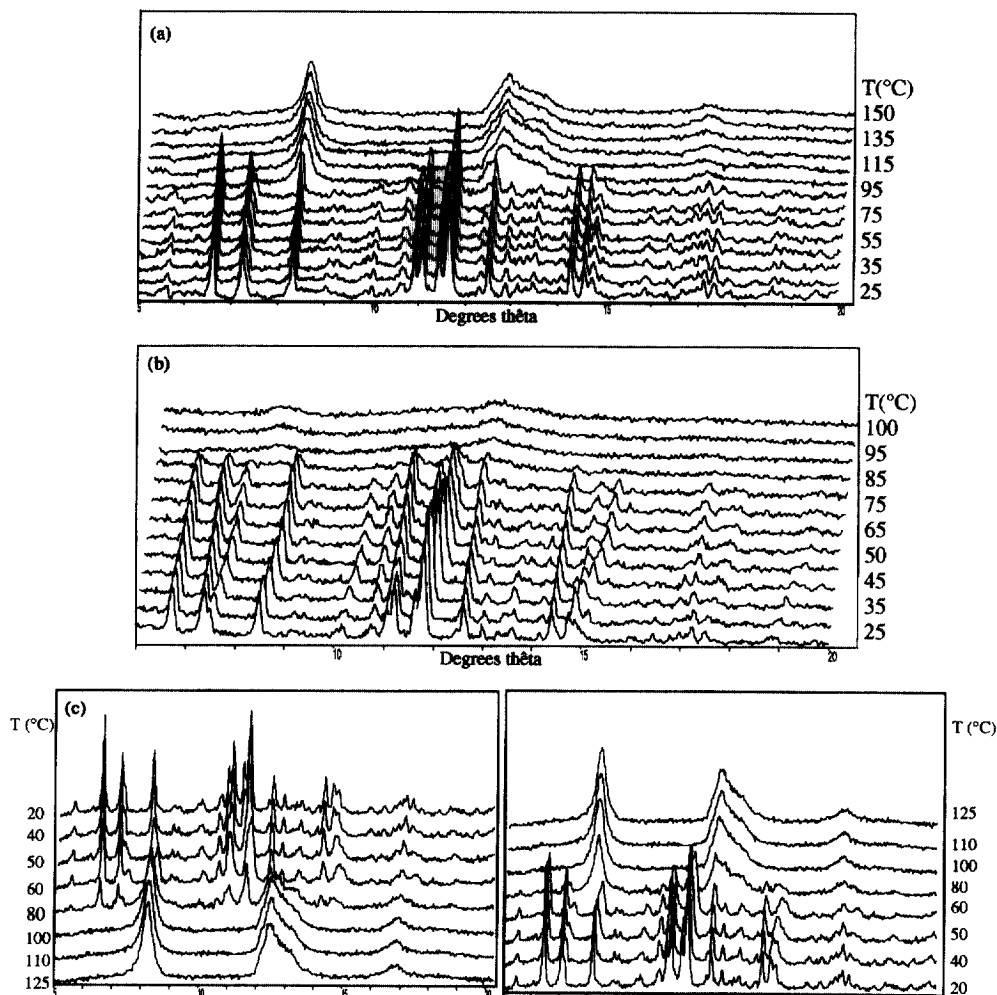


Fig. 7. (a) X-ray diffraction pattern of the dehydration of  $\text{UO}_2\text{F}_2 \cdot 1.5\text{H}_2\text{O}$  recorded as a function of temperature in ambient air. (b) X-ray diffraction pattern of the dehydration of  $\text{UO}_2\text{F}_2 \cdot 1.5\text{H}_2\text{O}$  recorded as a function of temperature under vacuum. (c) X-ray diffraction pattern of the dehydration of  $\text{UO}_2\text{F}_2 \cdot 1.5\text{H}_2\text{O}$  recorded as a function of temperature under an atmosphere of nitrogen.

The lower the water vapor pressure, the greater the number of steps observed. They correspond to the dehydration of solid solution  $\beta$ , to the transformation of  $\beta$  to  $\alpha$ , and to the loss of water from  $\alpha$ .

It is difficult to explain the complete absence of the  $B''$  and  $B'''$  regions, distinguished on thermogravimetric curves, on the C.R.T.A. curves obtained under water vapor pressure above  $10^{-2}$  mbar. It may be considered that the 'careful heating' by C.R.T.A. is a factor favorable to the metastable conservation of water molecules in the structure of phase  $\beta$ .

### 3.3. X-Ray diffraction

X-ray diffraction carried out as a function of temperature provides additional information. Fig. 7a, b and c represent the X-ray diffraction patterns of compounds following experiments performed in ambient air, under vacuum, and under an atmospheric pressure of nitrogen. These results provide no evidence for an intermediate compound between  $\beta$  and  $\alpha$ .

Recording data at atmospheric pressure (Fig. 7a) as a function of temperature shows the transition from  $\beta$  to  $\alpha$  at

95°C in accordance with thermogravimetric analysis. This transition occurs without significant variation of the composition of the phase  $\beta$  although a slight shift of the diffraction peak situated at  $7.32^\circ$  (at 25°C) to a shoulder of that at  $7.4^\circ$  is seen. This line is observed at  $7.36^\circ$  on heating to 95°C.

In the experiment carried out under vacuum (Fig. 7b), the shift of this last diffraction peak is much more pronounced and a shift of the line situated at about  $15^\circ$  is also discernible.

This phenomenon corresponds to the variation of the water composition of the solid solution  $\beta$ . The departure of water molecules has the effect of reducing the volume of the unit cell and, in the X-ray diffraction pattern, of shifting the lines towards larger angle. This shift is not the same for all the diffraction peaks, due to a distortion caused by the departure of water molecules.

The same experiment has been carried out under atmospheric pressure of nitrogen (Fig. 7c), and the evolution observed is comparable to that occurring under vacuum. Consequently, it is not the decrease of the total pressure that is responsible for the departure of water molecules, but the variation of water vapor pressure.

Under nitrogen, at 80°C, it is possible to observe the superposition of the X-ray diffraction patterns characteristic of both the hydrate  $\beta$  and the anhydrous compound. At this temperature, the peaks of  $\beta$  situated at ca. 7.6 and 15° move towards smaller angles. In fact, the flow of nitrogen into the diffraction chamber is rather slow, and water molecules resulting from the transformation of  $\beta$  to  $\alpha$  are immediately reoccluded by unchanged grains of  $\beta$ . This observation shows the importance of the water vapor pressure on the dehydration reaction.

#### 4. Conclusion

The study of the dehydration of  $\beta$ - $\text{UO}_2\text{F}_2$ , the stable hydrate of uranyl difluoride under usual conditions of temperature, pressure and hygrometry, has been carried out using a combination of X-ray diffraction, thermogravimetry and C.R.T.A. measurements.

No intermediate compounds are formed during the dehydration reaction. Water vapor pressure is an essential factor in this reaction.

It is possible to observe loss of water from  $\beta$  without significant structural change before the transformation of  $\beta$  to  $\alpha$ . This enables us to confirm that  $\alpha$  and  $\beta$  are two solid solutions.

The upper limit of the range of existence of the phase  $\beta$  is  $\text{UO}_2\text{F}_2 \cdot 1.55\text{H}_2\text{O}$  [20]. The lower limit is  $\text{UO}_2\text{F}_2 \cdot 1.2\text{H}_2\text{O}$ . These values agree roughly with those found by C.R.T.A.

For the  $\alpha$  phase, the results enable us to situate the upper limit at about  $\text{UO}_2\text{F}_2 \cdot 0.4\text{H}_2\text{O}$ .

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