THERMOGRAVIMETRIC BEHAVIOR OF SOME URANIUM COMPOUNDS — APPLICATION TO O:U RATIO DETERMINATION

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RESUMO

Estudou-se o comportamento termogravimétrico dinâmico dos vários compostos de urânio produzidos no IEA. A pirólise dêstes compostos ao ar e a análise do termograma respectivo possibilita o estudo comparativo dos mesmos. Exemplificando: é possível, pela inspeção das curvas termogravimétricas, dizer se um diuranato de amônio (DUA) foi obtido a partir da precipitação de uma solução de nitrato ou sulfato de uranila. Os termogramas mostram também a tendência de um certo óxido UO_2 (proveniente da redução de DUA por hidrogênio ou da redução de U_3O_8 por hidrogênio) ser pirofórico. As curvas de óxidos UO_2 pirofóricos e não pirofóricos são bastante distintas. Por outro lado também é possível, por meio da análise termogravimétrica dinâmica, acompanhar a evolução da auto-oxidação de um UO_2, pirofórico ou não, mantido no ar, durante o seu envelhecimento.

Principalmente no estudo dos óxidos reduzidos (UO_2) procurou-se explorar melhor os termogramas. A análise dos mesmos possibilita a determinação do conteúdo de urânio total através do ganho de massa (oxigenação do UO_2 a U_3O_8) e a relação O:U tem sido determinada rotineiramente pela queima ao ar de amostras de 1 a 2 gramas de UO_2 numa termobalança tipo Chevenard. Assim é pos

sível, pelo estudo de uma única curva termogravimétrica, determinar o conteúdo de urânio total e a % de U-IV na amostra, calculando-se a % de U-VI por diferença e estabelecer então a relação O:U num óxido $UO_{2 \pm x}$. Os resultados de muitas análises por êste processo têm sido acumulados durante 2 anos e comparados com a determinação da relação O:U pelos métodos convencionais, i.e., urânio total determinado volumètricamente após redução no redutor de Jones e titulação com dicromato de potássio e U-VI determinado polarogràficamente, calculando-se o teor de U+IV por diferença.

RÉSUMÉ

On a étudié le comportement thermogravimétrique dynamique des différents composés d'uranium produits à l'IEA. La pyrolyse de ces composés à l'air et l'analyse du thermogramme respectif, rendent possible l'étude comparative de ces composés.

Par exemple: par l'examen des courbes thermogravimétrique on peut affirmer si un diuranate d'ammonium a été précipité à partir d'une solution de nitrate ou de sulfate d'uranyle. Les thermogrammes montrent aussi la tendance d'un certain oxyde d' UO_2 (provenant de la réduction de l'U_3O_8 par l'hydrogène ou de la réduction de DUA par l'hydrogène) d'être pyrophorique. Les courbes des oxydes UO_2 pyrophoriques et non pyrophoriques sont assez distinctes.

Il est aussi possible à l'aide de l'analyse thermogravimétrique dynamique de suivre l'évolution de l'auto-oxydation d' un UO_2 pyrosphore ou non, laissé à l'air pendant son vieillissement.

On a beaucoup exploré les thermogrammes surtout dans l'étude des oxydes réduits (UO_2).

L'analyse des thermogrammes rend possible la détermination du contenu d'uranium total, par le gain de masse (Oxygénation de l'UO_2 à U_3O_8) et la relation U:O a été déterminé regulièrement en brûlant à l'air des échantillons d'un à deux grammes d'UO_2 dans

une thermobalance Chevenard.

De cette façon on peut déterminer par l'étude d'une seule courbe thermogravimétrique, le contenu total d'uranium et le pourcentage d'U-IV. Ensuite on calcule le pourcentage d'U-VI par différence et on établit alors la relation O:U dans un oxyde $UO_{2 \mp x}$.

Les résultates de plusieurs analyses par cette méthode ont été rassembles pendant deux années et comparés avec la relation O:U par les méthodes classiques, i.e, uranium total determiné volumétriquement après réduction au réducteur de Jones et titrage par le dichromate de potassium, et l'U-VI déterminé par polarographie. Le contenu d'U-IV est calculé par différence.

SUMMARY

This work presents the results of more than two years cumulative thermogravimetric experiences with uranium compounds produced at the Instituto de Energia Atômica, S.Paulo, Brazil.

The thermogravimetric behavior of ammonium diuranate (ADU) samples allowed to conclude that a certain sample represented an ADU precipitated from nitrate or sulfate solution, or permited to know about the pyrophoricity of some uranium dioxides obtained by the thermal reduction of ADU in hydrogen atmosphere. Both thermogravimetric diagrams for UO_2 samples, pyrophoric and normal (non-pyrophoric) are quite different; the thermogram for the pyrophoric one indicated a more complicated behavior. Therefore, it is possible to recognize a pyrophoric oxide by inpection of its thermogravimetric curve.

From the analytical point of view this paper outlines a procedure for the determination of the oxygen-to-uranium atomic ratio in uranium dioxide samples using only their thermograms obtained by the oxidative pyrolysis in air.

The oxygen to uranium ratio of a great number of uranium oxides was determined by thermogravimetric technique. The O:U ratios were checked periodically by the polarographic determination of the U-VI content or the O:U ratio was determined gravimetrically by simply heating the uranium oxide in a common furnace to U_3O_8 till constant weight. The O:U ratio determined by these different techniques normally was in good agreement.

On the other hand, a series of thermograms recorded for samples of the same batch of uranium dioxide gave valuable information on the stability of the oxide during aging.

INTRODUCTION

One of the main application of the thermogravimetric technique has been the investigation of the thermal stability of various materials and to find a suitable drying temperature for the investigation of a better weighing form of an element. Thousands of precipitates and compounds have been extensively investigated by thermogravimetry. Both thermogravimetry and differential thermal analysis have found many application in various fields, particularly in organic, inorganic and analytical chemistry. The dinamic nature of the thermogravimetric technique can be applied as an analytical method, and the possibility of using thermogravimetric together with others techniques such as polarography and X-ray make it more promissing.

In this work we are presenting the results of more than two years cumulative thermogravimetric experiences with uranium compounds produced at the "Instituto de Energia Atômica," São Paulo, Brazil.

Thermogravimetric behavior of ammonium diuranate (ADU) samples allowed to make comparison andconclude that a certain sample represented one ADU precipitated from nitrate or sulfate solution, or permited to know about the pyrophoricity of some uranium dioxides obtained by the thermal reduction of ADU in hydrogen atmosphere. Both thermogravimetric diagrams for UO_2 samples, pyrophoric and normal (non-pyrophoric) are quite different; the thermogram for the pyrophoric one indicated a more complicated behavior. Therefore, it is possible to recognize a pyrophoric oxide by inspection of its thermogravimetric curve.

From the analytical point of view this paper outlines a procedure for the determination of the oxygen-to-uranium atomic ratio in uranium dioxide samples using only their thermograms obtained by the oxidative pyrolysis in air.

On the other hand, a series of thermograms recorded for samples of the same batch of uranium dioxide gave information on the stability of the oxide during aging. Such information is valuable mainly to the Nuclear Metallurgy Division engineers whom are producing uranium dioxide, from ammonium diuranate salt, and storing it for fuel elements fabrication at the I.E.A..

APPARATUS

A recording thermobalance type TBM/A-Chevenard System (S.A.D.A.M.E.L., La Chaux-De-Fonds, Suisse) was used for the thermogravimetric examination of all samples. The sensitivity of the apparatus was such that a 60 mg variation of mass corresponded a displacement on the graph of 220 mm. The furnace can be operated for a maximum temperature of 1050°C (exceptionally 1300°C). The weights were recorded on a single chart (mm paper) and the weight scale covered a range of about 50-60 mg, each division (1mm) representing 0.27 mg. The temperature of the furnace was closely controlled to give a linear heating-rate of approximately 150°C/

/hour. The temperature control was achieved via a thermocouple and a pyrometer. Starting from room temperature, about 6.5 hours were required to reach 1000° C. The chart speed was such that the recording drum made one revolution in 24 hours. All samples were thermogravimetrically studied in air atmosphere.

CORRECTION

a) The buoyancy effect

An empty crucible, when heated in the furnace, apparently increases in weight. This is owing to the furnace atmosphere becoming less buoyant as its density decreases. The extent of this apparent change in weight is caused by several factors, including the size and shape of the crucible, the rate of heating, the temperature range used, air buoyancy, convection effects within the furnace, crucible geometry, radiation effects and the atmosphere in the furnace. For the same quartz crucible used in this work an increase of less than one mg was recorded between 20 and 1000° C. Therefore, for the balance and crucible used it was not necessary to apply a correction curve because the apparent weight change of the empty quartz crucible used was negligible.

b) Crucible

Throughout this work the same quartz crucible, open conventional type, weighting 4,01 g, was used.

SAMPLES

In this work we studied the behavior of various powdered samples of ammonium diuranate (ADU) and uranium dioxides ($UO_{2 \pm x}$). The sample weight varied from 0.5 to 2.0 g. The history of each sample and its preparation technique as for instance the NH_3 precipitation of ADU was reported.

THERMOBALANCE CONTROL

In order to check the performance of the balance once in a while the thermogravimetric curves of known standards compounds were recorded. Samples of the same batch of calcium oxalate monohydrate[1] and copper sulphide[2] were used for this. Figure 1, curve (1), shows the typical pyrolysis curve of calcium oxalate monohydrate. The value of the atomic weight for element C calculated directly from this thermogram was 12.016. The thermogram (2) of figure 1, recorded for copper sulphide precipitated by thiosulphate according Girard[2] is characteristic.

AMMONIUM DIURANATE (ADU)

ADU samples of nuclear grade purity fabricated by the Radiochemistry Division at the "Instituto de Energia Atômica" (I.E.A.) were used.

Two types of ADU were studied. The first type (sulphate system) was the ADU obtained by the NH_3 precipitation, bubbling the gas into a hot uranyl sulphate solution (60 g/liter in U_3O_8). This uranyl solution came from the elution of a cationic ion exchange column loaded with uranyl ion; the eluent used was a M ammonium sulphate solution of pH 1.8. The introduction of the NH_3 gas into the solution started when the temperature was about 50°C and continued untill precipitation of uranium was complete, when the temperature was mantained at 90-95° C. The precipitate had good crystaline characteristics and excelent filtrability and was dried at 100-110° C during 24 hours in an air oven. Figure 2 shows the representative pyrolysis curves of such one ADU. Thermogram (1) is an ADU (sulphate system) precipitated with 3% EDTA (ethylenedinitrilotetraacetic acid) added before introduction of NH_3 gas, and thermogram (4) is an ADU precipitated without addition of EDTA.

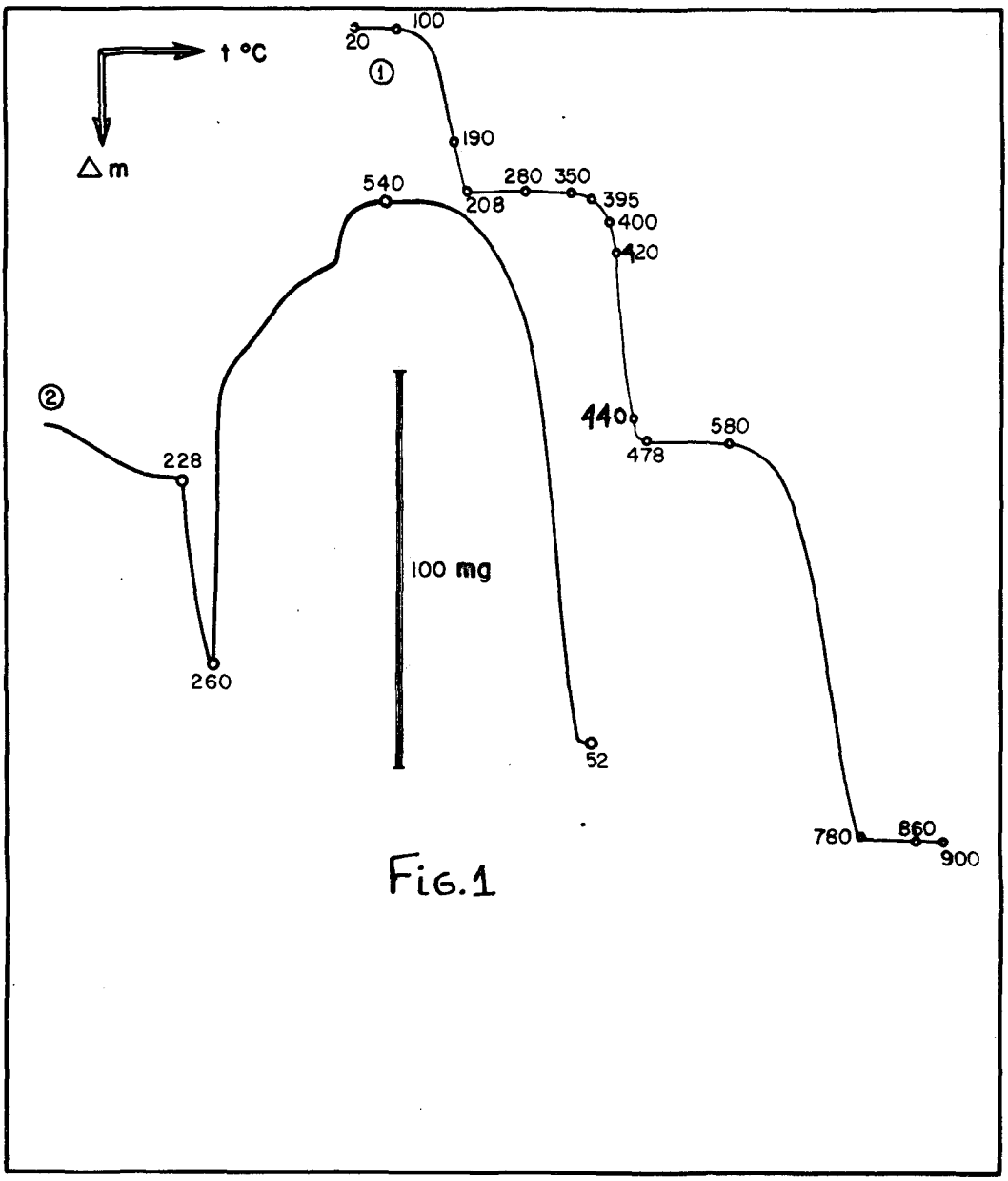

Fig. 1

Fig. 1 Pyrolysis curves of:

(1) calcium oxalate monohydrate

(2) copper sulphide

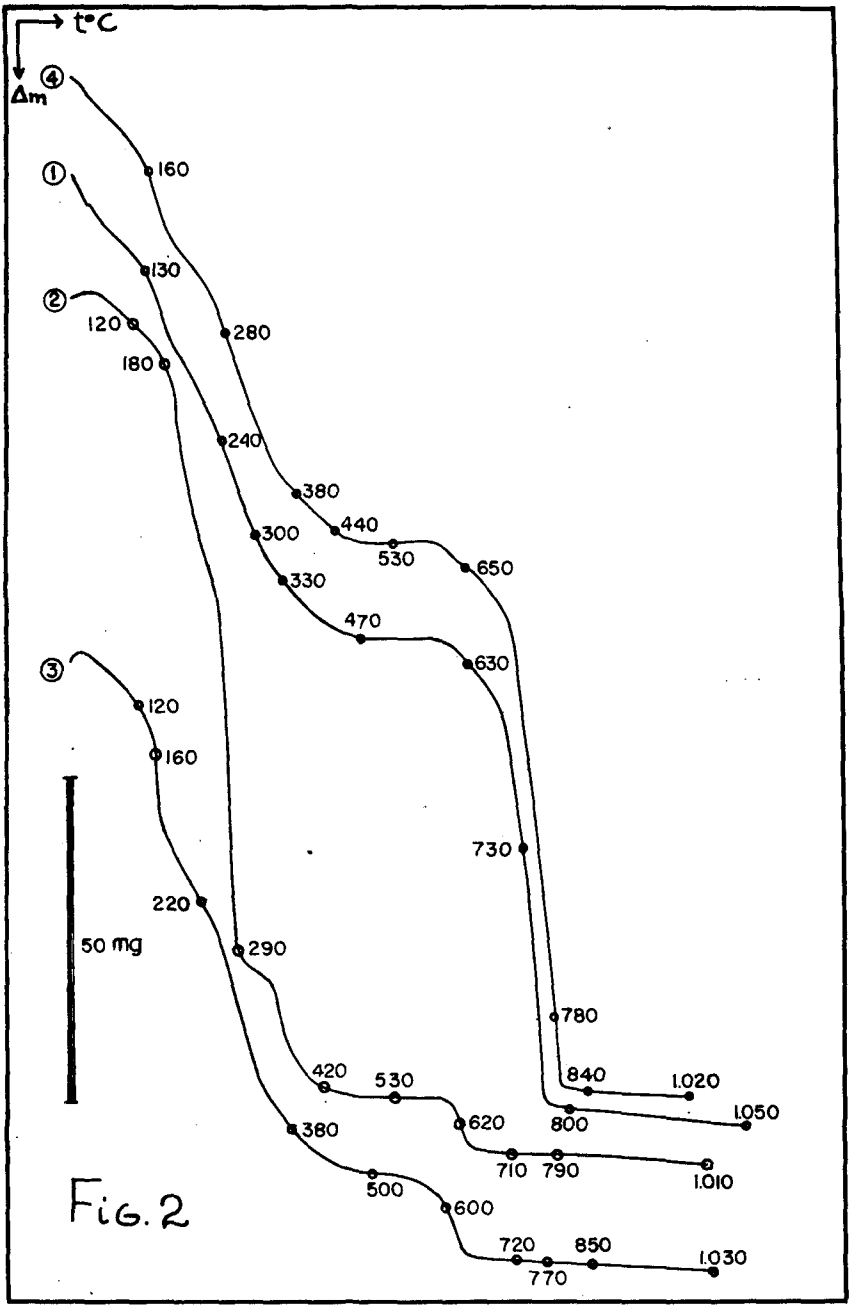

Fig. 2 Thermogravimetric curves of ADU.

(1) ADU (sulfate system) precipitated in the presence of 3% EDTA.
(4) ibid., without EDTA.
(2) ADU (nitrate system) precipitated in the presence of 3% EDTA.
(3) ibid., without EDTA.

The second ADU type (nitrate system) used was one obtained by the precipitation of an uranyl nitrate solution prepared by the elution of a cationic resin loaded with uranyl ion where the eluent was a 0.8M MH_4NO_3-0.3M HNO_3 solution. The filtered ADU was dried in the same way as the ADU for the sulphate system. Figure 2 shows the thermograms of ADU nitrate system, curve (2) representing an ADU precipitated in the presence of 3% EDTA and curve (3) without EDTA.

The difference between both types (nitrate and sulphate systems) was evident. The thermograms showed that the decomposition started slightly above room temperature and that practically constant weight was attained at lower temperature for the ADU nitrate system.

Figure 3 shows the thermogram of an ADU sulphate system and the corresponding derivative curve.

URANIUM DIOXIDE

a) Normal Oxide

The $UO_{2 \pm x}$ samples studied in this paper were obtained by direct reduction of ADU (sulphate system) or U_3O_8 in hydrogen at 700-770° C. The U_3O_8 oxides were prepared by calcination of ADU (sulphate system) at 850° C. All the reduced oxides were prepared by the I.E.A.'s Nuclear Metallurgy Division, using the ADU fabricated by the Radiochemistry Division.

Figure 4, curve A, is the thermogram of an uranium dioxide produced by the reduction of U_3O_8 in hydrogen atmosphere at 770° C, removed from the furnace and maintained in CO_2 gas atmosphere for cooling. This is the shape of a normal UO_2 oxide, with good metallurgical characteristics for uranium dioxide pellets fuel elements fabrication and having one oxygen-to-uranium atomic ratio very close to the theoretical one. This thermogram showed first a

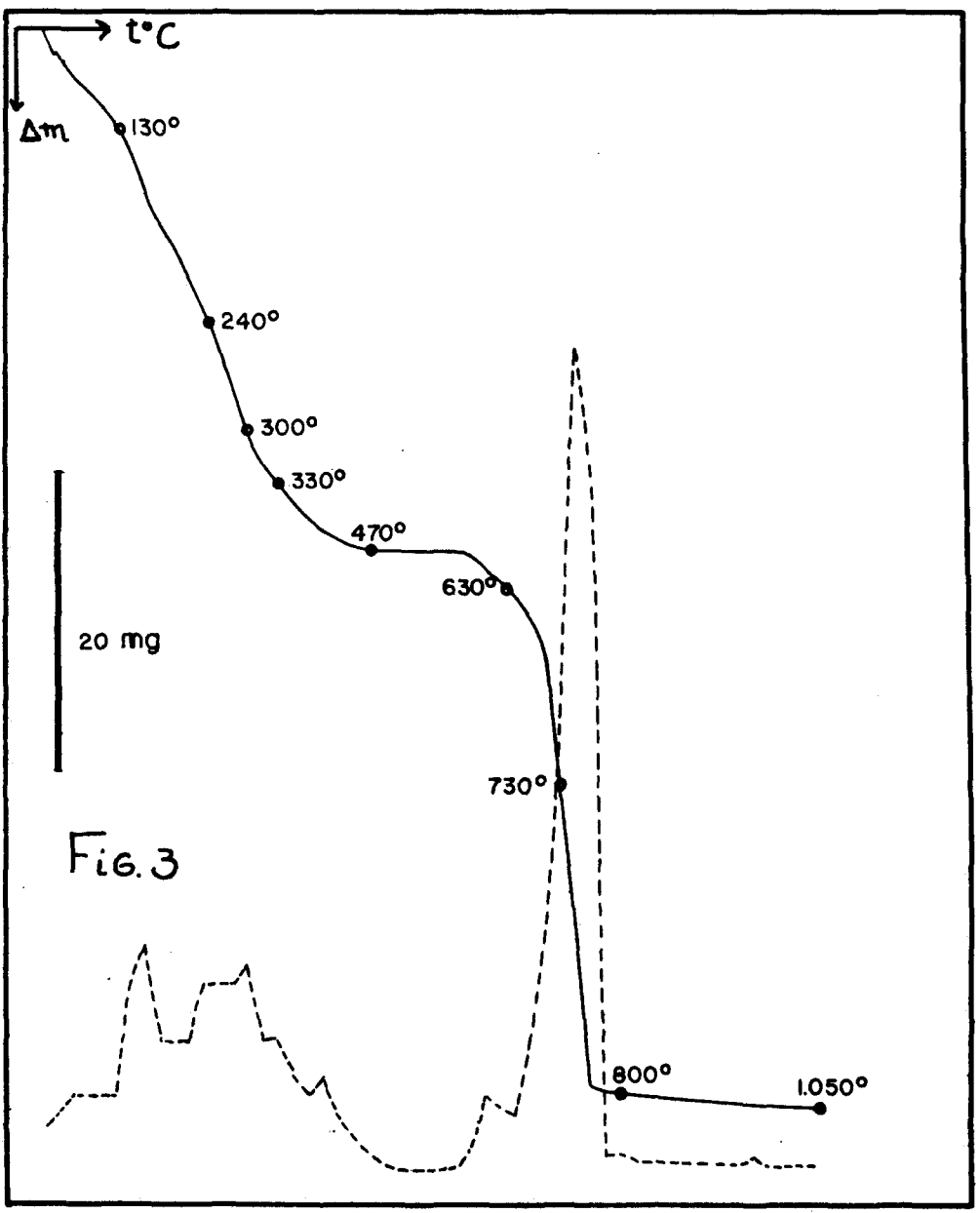

Fig. 3 Pyrolysis curves of ADU (sulfate system) and its derivative curve (doted line).

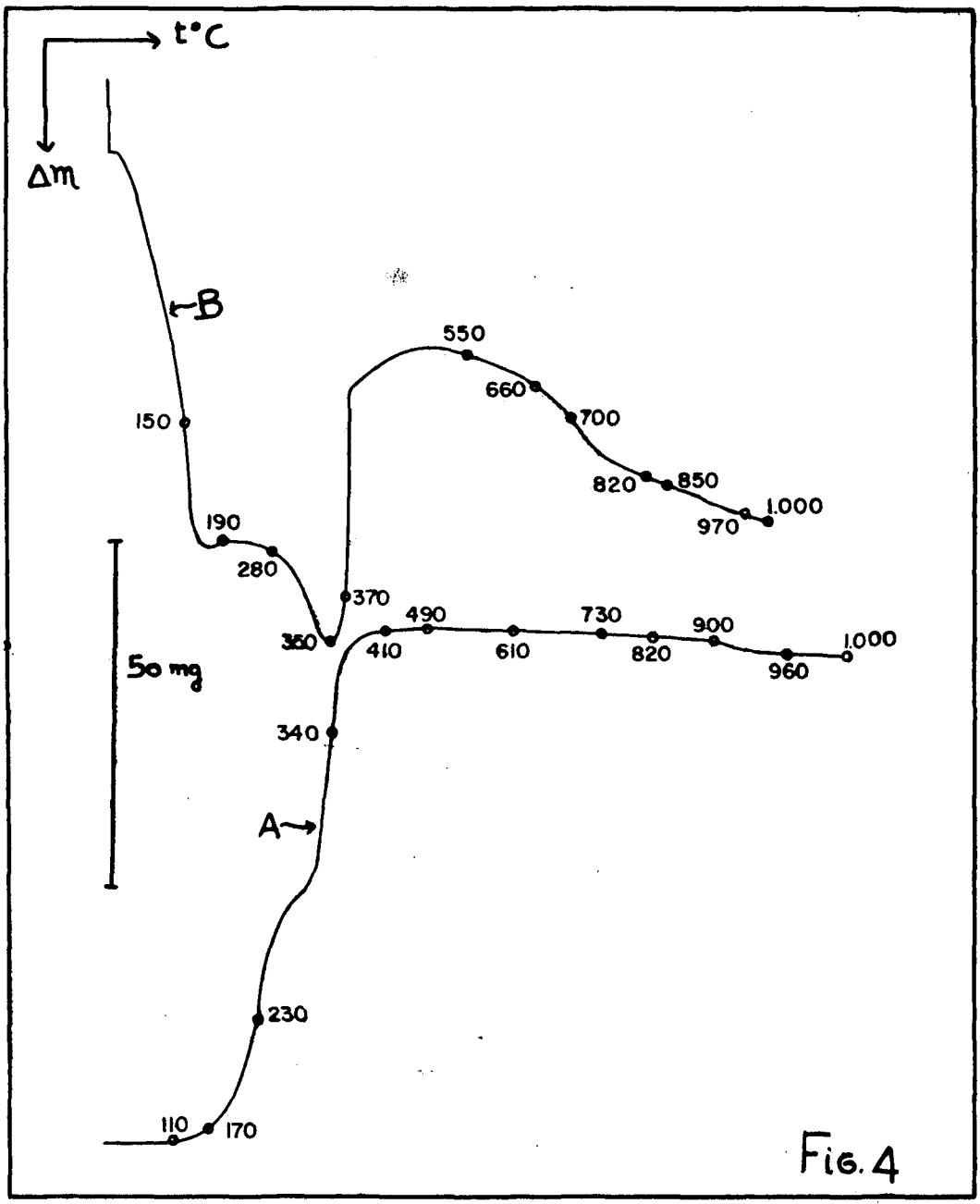

Fig. 4 Thermogravimetric curves of uranium dioxide
(A) UO_2 (normal) obtained by reduction of U_3O_8 in H_2 at 770° C.
(B) UO_2 (pyrophoric) obtained by direct reduction of ADU in H_2 at 770° C.

plateau in the range 20-110°C, then a gain in weight started and passed by an inflection point and finally a second plateau in the range of temperature of 410-900°C was attained. This is the type of thermogravimetric curve for an uranium dioxide considered as being excellent for the fabrication of UO_2 pellets fuel elements at the I.E.A.. This is the common, normal and characteristic thermogram encountered routinely for the uranium dioxide fabricated at the I.E.A.'s Nuclear Metallurgy Division. We have used thermograms like this for the determination of oxygen-to-uranium atomic ratio.

b) Pyrophoric Oxide

Figure 4, (B), is the pyrolysis curve of an uranium dioxide obtained by the direct reduction of ADU in hydrogen atmosphere at 770° C. This thermogram, on the other hand, indicates a more complicated behavior, showing first a weight loss between 20 and 350° C, then in the 350-500°C range a gain in weight and finally a second region of constant weight loss. We have found that uranium dioxides obtained by direct reduction of ADU very frequently were pyrophoric. This thermogram is characteristic of pyrophoric uranium dioxide.

While in the normal uranium dioxide, as the thermogram in Figure 4, (A), two waves passing through an inflection point are observed, in the pyrophoric uranium dioxide, Figure 4, (B), only the correspondent second (higher) wave is observed, or the first wave is very much minimized. This pyrophoric dioxide had an oxygen-to-uranium ratio of 2.49. Besides that, the normal oxide displays two plateaux in the 20-110° C and 400-900° C, while in the pyrophoric oxide the correspondent plateau were absent.

We have found that in the case of pyrophoric uranium dioxide the first (lower) wave is constantly diminished on aging when stored in air atmosphere at room temperature. This lower region of the thermogram could be completely absent, subsisting

only the second (higher) wave. This is due to the re-oxidation of the oxide and this oxidation occurs at lower temperature for the first wave than for the second one.

Figure 5, (A), is the thermogram of an uranium dioxide produced by the direct reduction of ADU in hydrogen at 770° C; thermograms (B) and (C) representing two uranium dioxides obtained by direct reduction of ADU in hydrogen atmosphere and cooled in CO_2 and thermogram (D) is correspondent to one uranium dioxide prepared by reduction of U_3O_8 in hydrogen at 770° C and cooled in CO_2, the U_3O_8 obtained by calcination of ADU at 850° C. The oxide of thermogram (D) had an normal behavior, while the oxides of curves (B), (C) and (D) exhibited different grade of pyrophoricity.

OXYGEN-TO-URANIUM RATIO DETERMINATION

The oxygen-to-uranium ratio of a great number of uranium oxides was determined by the thermogravimetric technique. The specimens were routinely determined by heating 1-2 grams samples in air to form U_3O_8 and following the weight increase with the thermobalance. This weight change was monitored to $\pm$ 0.2 mg, which corresponds to a change of $\pm$ 0.005 in the oxygen to uranium ratio. The O:U ratio determined by ignition to U_3O_8 in air were checked periodically by the polarographic determination of the U-VI content, or the O:U ratio was determined gravimetrically by simply heating the uranium oxide in a common furnace to U_3O_8 till constant weight. The O:U ratio determined by these different techniques normally was in good agreement. (Table I)

The determination of the oxygen-to-uranium atomic ratio was made by the examination of the recorded thermogravimetric curve. Observing, for instance, the thermogram of Figure 4, (A), the gain of weight is attained in such a way that two waves are recorded. The first wave (lower) corresponds to the oxidation of UO_2 to U_3O_7 and occurs in the temperature range of 170-270° C [3,4,5]. The

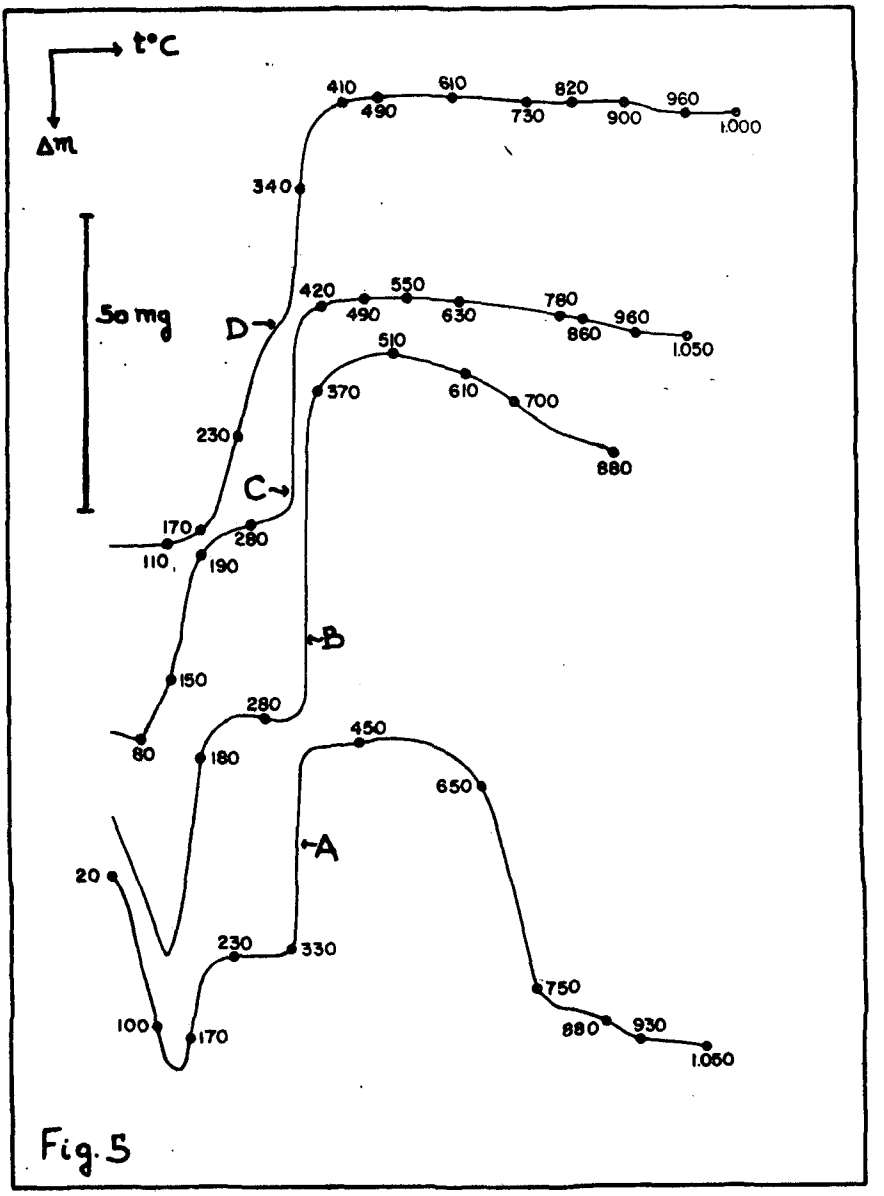

Fig. 5 Pyrolysis curves of uranium dioxide

(A) UO_2 (pyrophoric) obtained by direct reduction of ADU in H_2 at 770° C.

(B), (C) UO_2 prepared by direct reduction of ADU in H_2 and cooled in CO_2.

(D) UO_2 produced by reduction of U_3O_8 (ignition of ADU in air at 850° C) in H_2 at 770° C.

second wave (higher) corresponds to the oxidation of U_3O_7 to U_3O_8, being complete at 365° ± 15[3,4,5]. Finally a plateau is reached over the range 390-900° C, corresponding to the existence of an oxide stoichiometrically equal to U_3O_8.

In this work we assumed that for an uranium dioxide of very high purity when both waves, separated by the inflection point, had the same height, the oxide had a theoretical O:U atomic ratio value of 2.00. As the oxide was being more oxidized, the first wave was lowering while the second wave remained constant, and, consequently, the O:U ratio was becoming greater. When the first wave disappeared completely the oxide was such that corresponded to a mixture having only 50% UO_2. Therefore, it is possible to calculate the U-IV content (UO_2) by using the ratio of both waves.

Assuming the oxidation (gain of oxygen) of UO_2 to U_3O_8 in two stages, we have:

first wave, lower (i): $3\ UO_2 + O = U_3O_7$ ($=UO_{2,34} \pm 0.03$) at

170-270° C

second wave, higher (s): $U_3O_7 + O = U_3O_8$ ($=UO_{2,666}$) 365°C ± 15

URANIUM - IV

The uranium-IV content is calculated by:

$$\text{U-IV (\%)} = \frac{\text{total wave (i) + (s)}}{2\ (s)} \cdot 88.167$$

When (i) = (s), the ratio $\frac{\text{total wave}}{2\ (s)}$ is the unity, that is, the U-IV is maximum and theoretically equal to 88.167%. For a partially reoxidized oxide, the ratio $\frac{\text{total wave (t)}}{2\ (s)} < 1$ and the content of U-IV is less than 88.167%, corresponding to an

oxide of O:U atomic ratio greater than 2.00.

TOTAL URANIUM

The content of total uranium in the sample is calculated by the total gain of oxygen and is given by the total wave in the correspondent thermogram. Therefore, for a sample of initial mass m_1 and a gain of oxygen after the recorded thermogram Δm_o, the total uranium content is calculated by:

$$\text{Total Uranium (U-T \%)} = \frac{m_1 + \Delta m_o}{m_1} \cdot 84.799$$

HEXAVALENT URANIUM

The content of hexavalent uranium, U-VI, is calculated by the difference between total uranium and uranium-IV.

OXYGEN-TO URANIUM ATOMIC RATIO

O:U, is calculated by the relation

$$O:U = \frac{3\ \text{U-VI (\%)} + 2\ \text{U-IV (\%)}}{\text{U-T (\%)}}$$

RESULTS

Table I shows the results of some O:U ratio determination by the thermogravimetric technique suggested in this work. The thermogravimetric results are compared with others techniques, the analysis being made in the same day of the thermogram. In column G are the results of O:U ratio determined gravimetrically by calcination of 2-5 grams samples of oxide in air atmosphere furnace, starting from room temperature and raising the temperature slowly untill 800° C was reached and mantaining at this temperature

during 2 hours. In Column P,V are the results obtained by determining the total uranium content volumetrically with $K_2Cr_2O_7$ after reduction in a Jones reductor[6] and determining the U-VI by polarographic technique[7]. The polarographic determination of U-VI in uranium dioxides was made by the procedure of Burd and Goward[7] with the modification of using separan as suppressor of maxima[8].

STABILITY OF URANIUM DIOXIDE ON AGING

As was mentioned before the thermobalance can give information on aging of a certain uranium dioxide sample. Running a series of thermograms over a certain period for one stored oxide batch the auto-oxidation of the material could be estimate easily. This have a fundamental importance in the case of uranium dioxide pellets fuel elements fabrication, as is the case with the I.E.A. Nuclear Metallurgy Division.

Figure 6 shows a series of 4 thermograms recorded for equal mass o a reduced oxide in the following dates: (A) Nov. 28, 1963 - (B) April, 22, 1964 - (D) June 1, 1964 and (C) May 29, 1964. The uranium dioxide was prepared by reduction of ADU in hydrogen atmosphere at 770° C and cooled in CO_2. The obtained oxide was slightly pyrophoric. Thermograms (A), (B) and (D) corresponding to O:U atomic ratio of 2.02_2, 2.17_0 and 2.21_1 respectively and were recorded for this same uranium dioxide stored in a stoppered glass bottle in air atmosphere. Thermogram (C), corresponding to a O:U ratio of 2.28_0 was recorded for the same oxide after being mantained at 110° C during 1 hour in an air oven. By examination of the thermograms (A), (B) and (D) we can conclude that the oxide was slowly being oxidized and, as can be seen, their correspondents first waves (lower) were diminishing or their O:U ratio were increasing. A such oxide can not be heated even at as low temperature as 110° C without reoxidation.

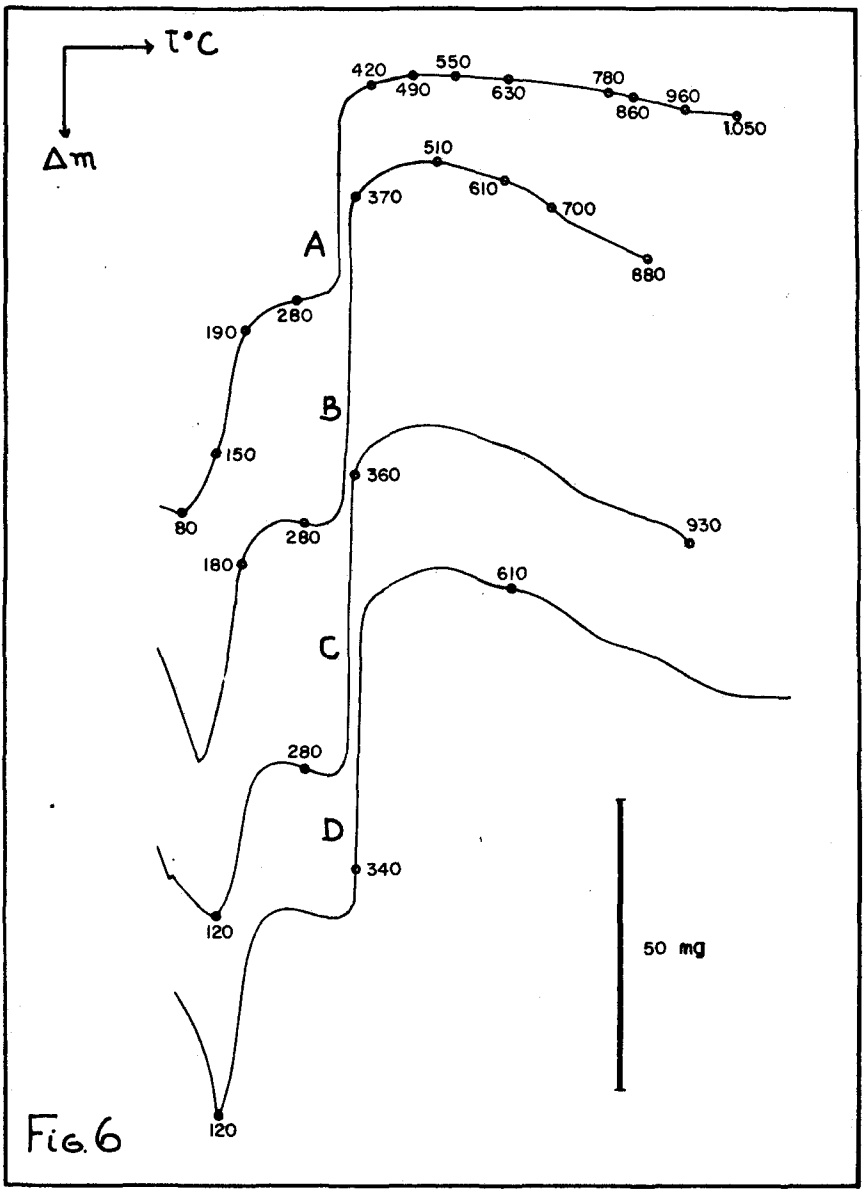

Fig. 6 Pyrolysis curves of same UO_2 on aging. Thermograms of equal mass of UO_2 (direct reduction of ADU) stored in glass bottle (air). Dates and U:O ratios for thermograms are:

(A) Nov. 28, 1963 - 2.02_2 (B) April, 22, 64 - 2.17_0

(C) May, 29, 1964 - 2.28_0 (heated in air oven, 1 hr).

(D) June, 1, 1964 - 2.21_1

Table II presents the results of a series of O:U ratio determinations via their thermograms obtained for the same uranium dioxide batch stored in stoppered glass bottle as powder in air atmosphere. The auto-oxidation is evident as can be seen by the increase in the O:U ratio on aging at room temperature.

The effect of heating the samples of the same uranium dioxide batch at temperature as low as 110° C in air was an increase in the rate of re-oxidation. The thermograms A, B, C, D and E of Figure 7 are correspondents to samples of the same batch of uranium dioxide recorded after mantaining the oxide in an air oven at 110° C during 1, 5, 24 and 48 hours, respectively. The correspondents O:U atomic ratio were determined as being 2.02_2, 2.28_0, 2.29_9, 2.44_9 and 2.48_9, respectively. The thermograms showed clearly that the first wave was lowering from A to E, while the second (upper) wave, that requires higher temperature for oxidation (U_3O_7 to U_3O_8) was not altered in all thermograms.

Figure 8 shows the thermograms of samples A, B, C, D (1.2051, 1.3913, 1.3911 and 1.3923 g, respectively) of the same powdered uranium dioxide batch (Nuclear Metallurgy Division UO_2 production batch for fuel elements fabrication), stored in a stoppered glass bottle, in air. This oxide was prepared by the reduction of U_3O_8 at 770° C in hydrogen atmosphere furnace, the reduced oxide cooled in CO_2. The U_3O_8 was prepared by calcination of ADU (sulphate system) at 850° C. The uranium dioxide was reduced in February 1, 1965 and the of recorded thermograms and correspondent O:U ratios were:

Oxygen: Uranium ratio

Thermogram	Date (1965)	Thermobalance	Gravimetry
A	Feb., 25	2.02_3	2.02_8 and 2.03_1
B	March, 16	2.01_5	2.02_0
C	March, 26	2.01_0	2.01_0
D	May, 5	2.03_5	2.02_6

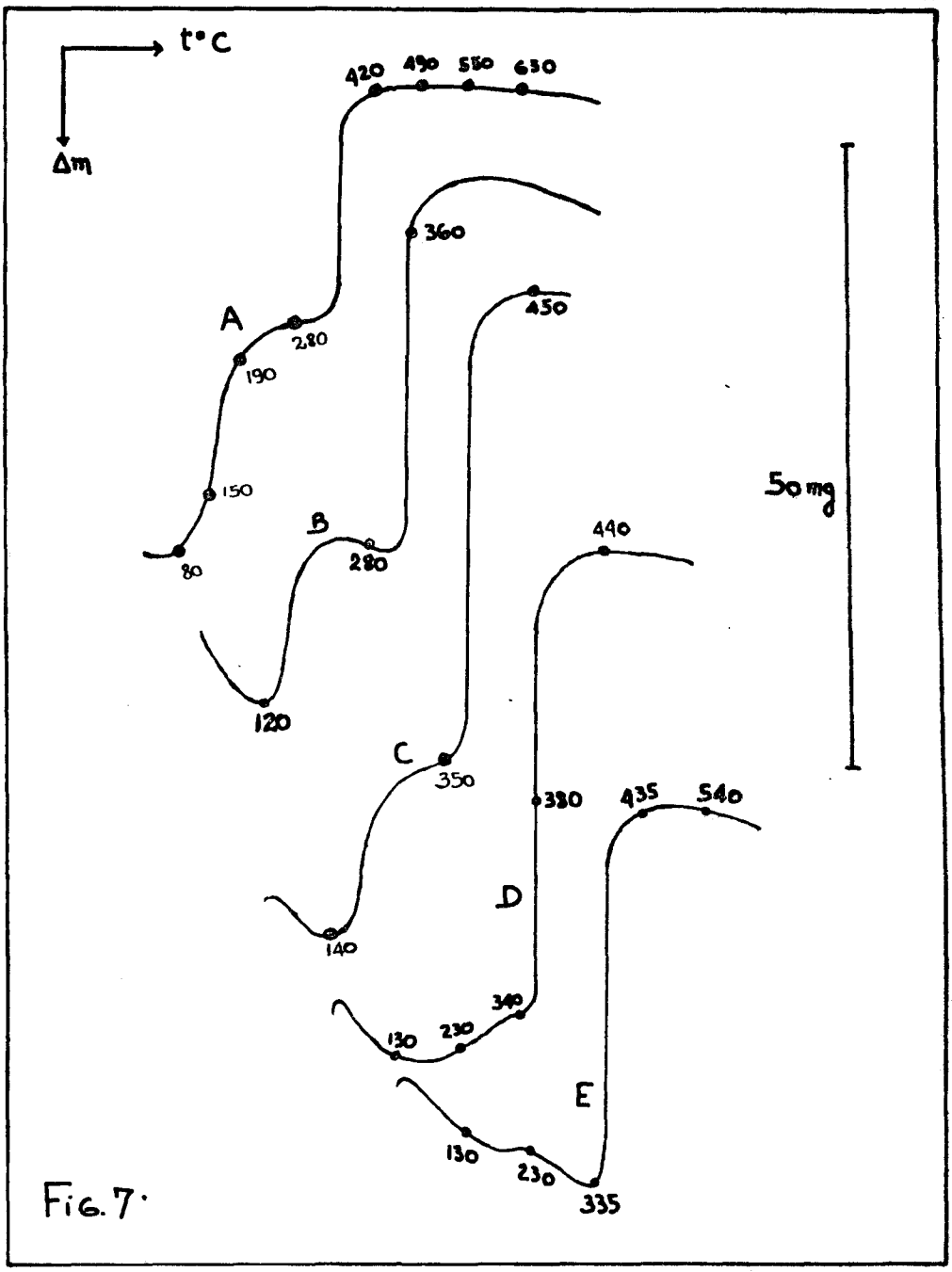

Fig. 7 Heating Effect (air, 110° C) or Uranium Dioxide.
Heating time (hours) and O:U ratios are:

(A) 0, 2.02_2 (B) 1, 2.28_0 (C) 5, 2.29_4
(D) 24, 2.44_9 (E) 48, 2.48_9

This uranium oxide (Figure 8) proved to be much more stable on aging in air atmosphere than the oxide obtained by direct reduction of ADU in hydrogen atmosphere (Figure 6).

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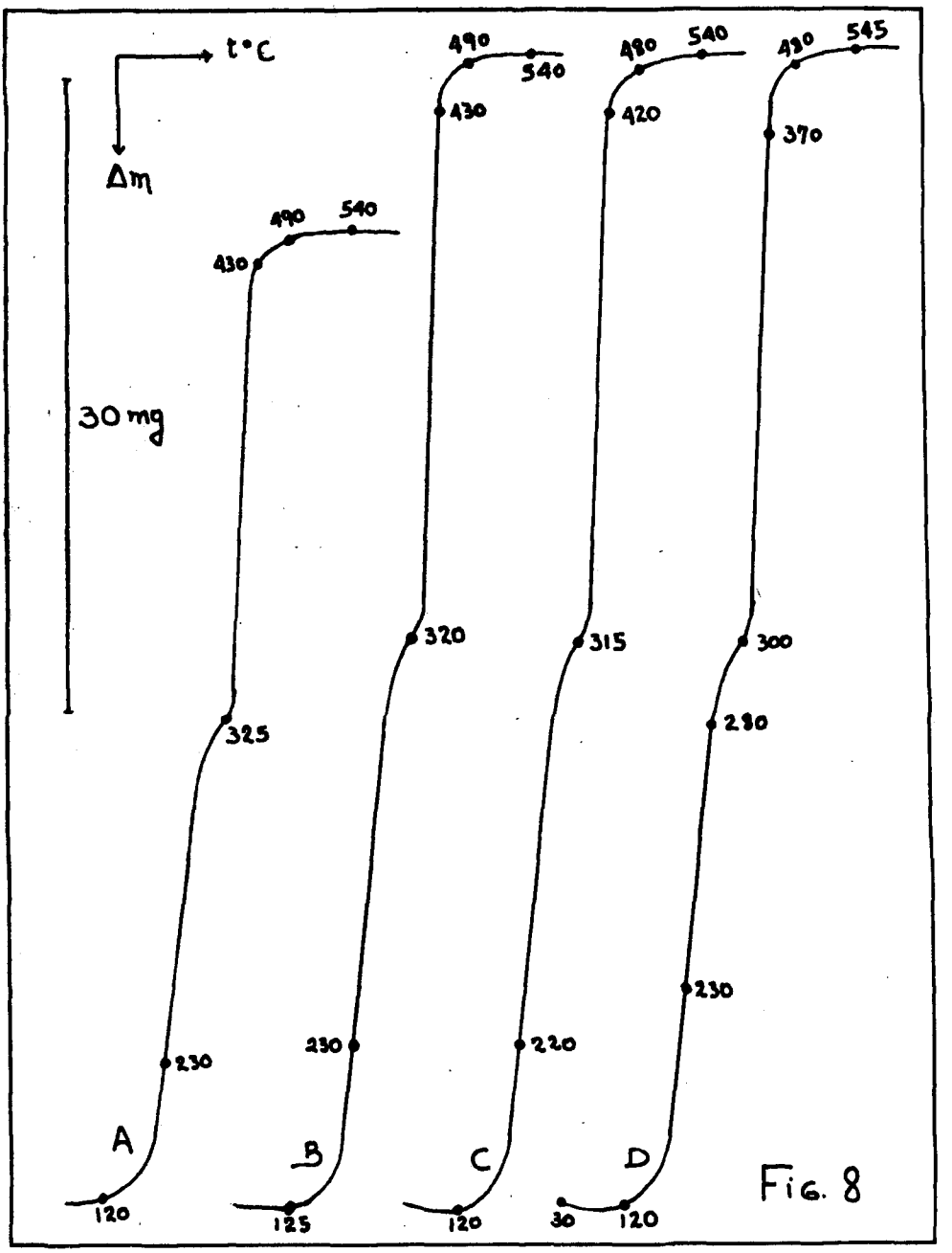

Fig. 8 Stability of Uranium Dioxide on aging in air.

Samples of same oxide obtained by reduction of U_3O_8 in H_2 and cooled in CO_2. Dates (1965) and O:U ratios are:

(A) Feb. 25 - 2.02_3 (B) March, 16 - 2.01_5

(C) March. 26 - 2.01_0 (D) May, 5 - 2.03_5

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TABLE I

Comparison of O:U ratios determined by different techniques					
Sample	History	Date of Analysis	O:U ratios T.B.	G.	P.V.
Am-26-2	ADU calcinated at 850° C and reduction at 770° C/hydrogen	XI.11.63	2.02_4	2.01_4 2.04_0 2.03_1	
		XI.19.63	2.01_1	2.01_7	2.02_5
UO_2-NOVO	Direct reduction of ADU in hydrogen and cooling in CO_2, in XI.27.63	XI.28.63	2.02_2	2.02_0	2.01_8
		IX.14.64	2.17_1	2.19_4	
		VI.17.64	2.16_4	2.16_6	2.17_7
		VI.18.64	2.16_3	2.16_8	2.16_3 2.16_7
		VII. 7.64	2.21_9	2.20_5	2.19_4
Am-15/64	ADU calcinated at 600° C 2 hrs. and reduced in hydrogen at 77° C	VII. 8.64	2.00_9	2.01_5	2.02_4
		VII.10.64	2.00_3	2.01_3	2.02_7
Am-16/64	UO_2 batch production	VII.24.64	2.00_0	2.00_5	2.02_0
		VIII. 4.64	2.00_0	2.00_6	2.02_0
Am-20/64	UO_2 batch production, reduction time, 10 min.	VIII.17.64	2.04_9	2.05_0	2.06_2

contd.

contd. of Table I

Sample	History	Date of Analysis	O:U ratios T.B.	G.	P.V.
Am-24/64	UO_2 batch production	VIII.27.64	2.01_1	2.01_5	2.02_5
					2.02_7
Am-25/64	UO_2 batch production	IX. 3.64	2.00_4	2.00_8	2.02_4
					2.02_2
Am-26/64	UO_2 batch production	IX. 4.64	2.01_7	2.01_9	2.02_5
					2.02_6
Am-S.4/65	U_3O_8 reduced in hydrogen in Jan. 25 to 30, 1965	II.24.65	2.02_0	2.03_2	2.03_5
				2.02_9	
Am-S.5/65	U_3O_8 reduced in hydrogen in Feb. 1 to 6, 1965	II.25.65	2.02_3	2.03_1	2.03_5
				2.02_8	
Am-S.6/65	U_3O_8 reduced in hydrogen in Feb. 8 to 13, 1965	II.26.65	2.00_4	2.02_0	2.02_5
				2.02_3	
				2.00_7	
		III.16.65	2.01_5	2.02_0	
			2.00_7	2.02_6	

T.B. = Thermobalance; G. = Gravimetry; P.V. = Uranium total by volumetric technique and U-VI by polarography

TABLE II

O:U Ratios Determination During Aging of the Same Batch Oxide

Sample: UO_2-NOVO, stored in stoppered glass bottle. Reduced in Nov. 27, 1963.

Date of analysis	O:U ratio Thermobalance
XI.28.63	2.02_2
XII. 3.63	2.02_2
IV.14.64	2.17_2
IV.20.64	2.16_5
IV.22.64	2.17_0
VI.17.64	2.16_4
VI.18.64	2.16_3
VII. 7.64	2.21_9

Sample: Same above, heated at 110° C in an air oven.

Heating time (hours)	Date of analysis	O:U ratio Thermobalance
0	XI.28.63	2.02_2
1	V.29.64	2.28_0
5	VI.19.64	2.29_9
24	VI.23.64	2.44_9
48	VI.26.64	2.48_7