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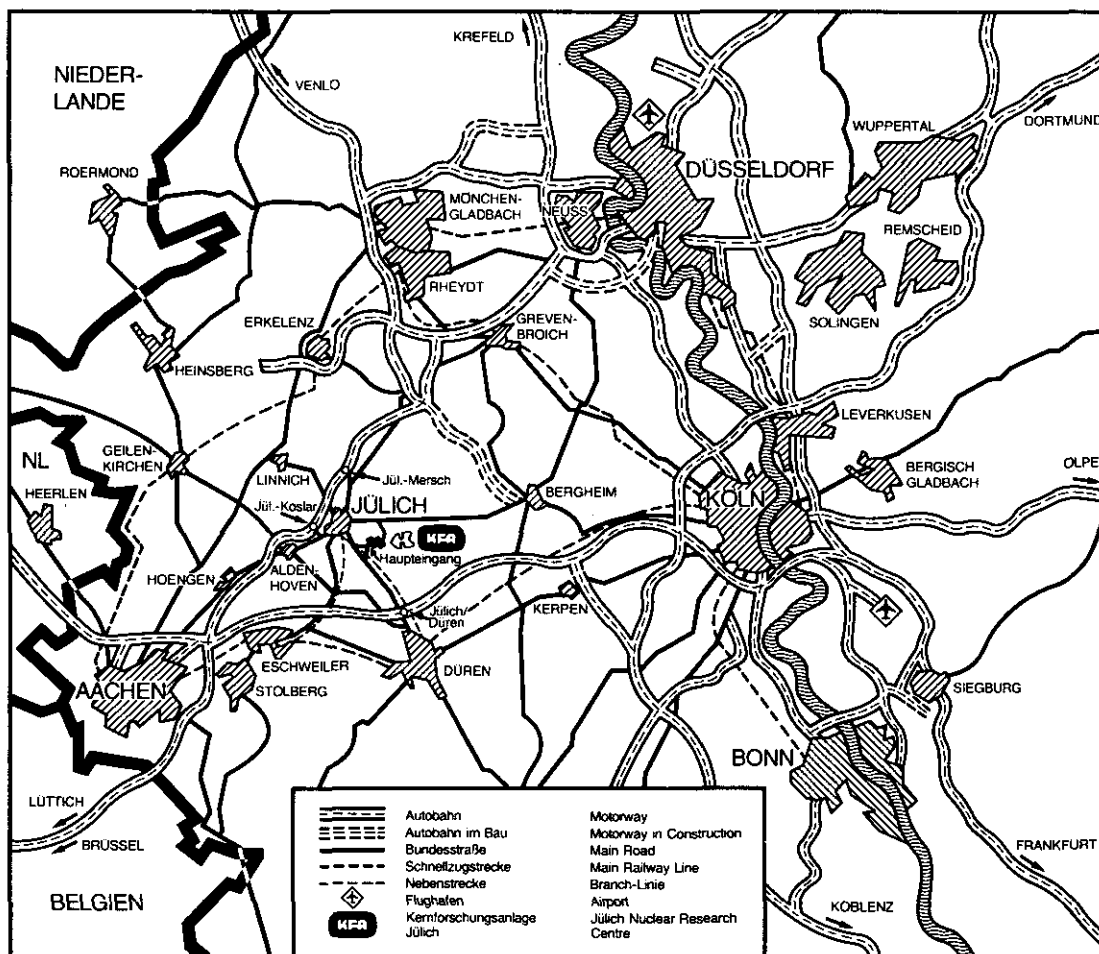
Zentralabteilung Brennelement- und Bestrahlungstechnologie

**METHODS OF DETERMINATION OF
OXYGEN-TO-URANIUM RATIOS IN
URANIUM DIOXIDE**

BY

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BY

A. S. ABDEL-HALIM, A. F. BISHAY, F. H. HAMMAD

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NUCLEAR METALLURGY DEPARTMENT

THIS WORK HAD BEEN PERFORMED UNDER THE JOINT RESEARCH
AND DEVELOPMENT PROJECT ON NUCLEAR FUEL DEVELOPEMENT
AND TESTING BETWEEN AEA-CAIRO AND KFA-JÜLICH.

JUNI 1983

ABSTRACT

Methods used for the determination of oxygen to uranium ratios has been collected and discussed. These methods are destructive and non destructive. The experimental procedures are written in form of manuals to help their easy use in nuclear fuel quality control laboratories. It is of special importance in nuclear fuel laboratories of the nuclear metallurgy department of ARE-AEA in connection with the R&D fuel programme conceived within the scope of German - Egyptian cooperation between the Jülich Nuclear Research Centre and the Nuclear Research Centre at Inchas, AEA - Egypt.

The accuracy and place of use of each method has been tabulated.

ملخص

ان الطرق المستخدمة لتحديد نسبة الاكسجين الى اليورانيوم في ثاني اكسيد اليورانيوم قد تم تجميعها ومناقشتها في هذا التقرير . . . وتنقسم هذه الطرق الى طرق اتلافية وطرق لا اتلافية . . . وقد تم عرض هذه الطرق بشكل تجريبي حتى يسهل استخدامها في معامل ضبط جودة الوقود النووي . . . في قسم الفلزات - مركز البحوث النووية بأنشاص لبرنامج بحوث وتطوير انتاج الوقود النووي مع مركز البحوث النووية بيوليس.

وقد تم جدولة هذه الطرق مع درجة دقة كل منها واماكن استخدامها .

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1- Introduction

Uranium dioxide is one of the major nuclear fuel materials now being used in nuclear power reactors. For light water (LWR) and heavy water reactors (HWR), sintered uranium dioxide pellets with a density of about 95% of the theoretical density (TD) have been used as a nuclear fuel. Sintered uranium dioxide microspheres with diameter between 0.01 and 1 mm may be utilized either for the preparation of vibro-compacted fuel element for both light water and fast reactors (sphere Pac fuel element type)⁽¹⁾ or for the production of fuel elements with coated particles for high temperature gas cooled reactors (HTGR)⁽²⁾.

One of the main characteristics of uranium dioxide is the ease of inclusion of excess oxygen in its cubic lattice to give a non-stoichiometric oxide of composition UO_{2+x} ($x = 0 - 0.25$). It has been established that the presence of non-stoichiometric oxygen is undesirable (due to its effect on the performance of UO_2 under irradiation)⁽³⁾; grain growth takes place more readily than with stoichiometric material irradiated under comparable conditions, and the release of fission products is considerably higher. It has also been found that an increase in the O/U ratio brings a marked decrease in the thermal conductivity of uranium dioxide⁽⁴⁾. Therefore the determination of the O/U ratio is an important quality control aspect of UO_2 nuclear fuel.

Several destructive and non-destructive methods for the determination of O/U ratio have been developed. Destructive methods include thermogravimetric, polarographic, titrimetric and coulometric procedures, while the non-destructive methods are the X-ray diffraction and the measurement of electromotive force of a Ni, NiO electrolyte - UO_{2+x} cell. These methods have been reviewed by Florence⁽⁵⁾.

In this report all existing methods used for determination of O/U ratio in various laboratories across the world are reviewed and collected. The experimental procedures are written in form of manuals to help their easy use in nuclear fuel quality control laboratories. It is of special importance on nuclear fuel laboratory of the nuclear metallurgy department of ARE-AEA in connection with the R & D fuel programme conceived within the scope of German-Egyptian cooperation between the Jülich Nuclear Research Centre and the Nuclear Research Centre at Inshas, AEA-Egypt.

2. Background information on the U-O system and importance of O/U ratio:

The uranium oxygen system is one of the most complicated of the binary systems. This is not only due to the existence of a large number of oxide phases, but also to the fact that deviation of stoichiometry are more the rule than the exception. The existence of four thermodynamically stable oxide phases, UO_2 , U_4O_9 , U_3O_8 and UO_3 , have now been well established, as shown in Fig. 1. In addition to these, several metastable phases such as the U_3O_7 and U_2O_5 ⁽⁶⁾ phases have been reported.

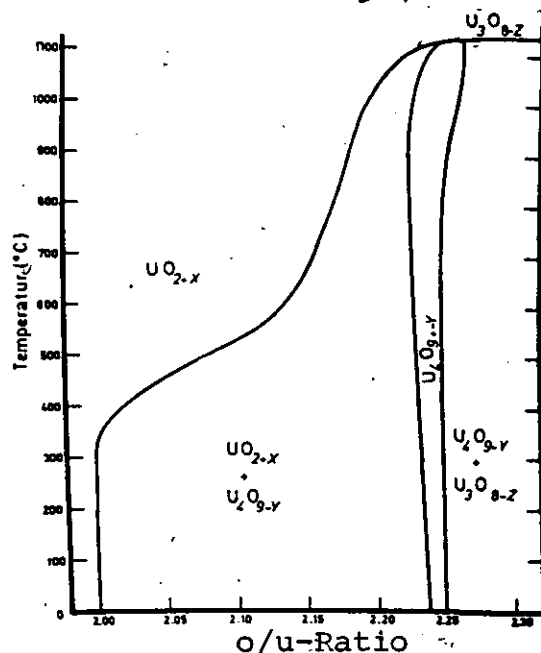


Fig. 1: Phase diagram of the uranium-oxygen system.

The most important phase in the system is uranium dioxide UO_2 . It is generally agreed that the UO_2 phase does not extend below the composition $\text{UO}_{2.00}$ at moderate temperatures (say below 1000°C). At room temperature, and up to at least 300°C oxygen fails to enter the UO_2 structure to form stable solid solutions. At higher temperatures oxygen does penetrate the UO_2 lattice interstitially to give material of the composition UO_{2+x} , in which the value of x depends on the temperatures, the surface area of the oxide and the partial pressure of oxygen. The limiting value of x , at which UO_{2+x} is in equilibrium with the U_4O_9 phase, increases with temperature to a value of 0.17 at 950°C and 0.244 at 1123°C , the highest temperature at which the U_4O_9 phase can exist⁽⁷⁾. Above that temperature the limiting value of x , given by the equilibrium between UO_{2+x} and U_3O_{8-2} increases gradually.

Uranium dioxide has a face-centered cubic structure (fluorite type) with lattice parameter $a = 5.470 \text{ \AA}$ at the stoichiometric composition⁽⁸⁾. The elementary cell is face-centered with respect to the uranium ions, with the oxygen ions at $\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$ sites. The unit cell contains four molecules of UO_2 as well as four interstitial sites at $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$ equidistant from the eight oxygen atoms as shown schematically in Fig. 2.

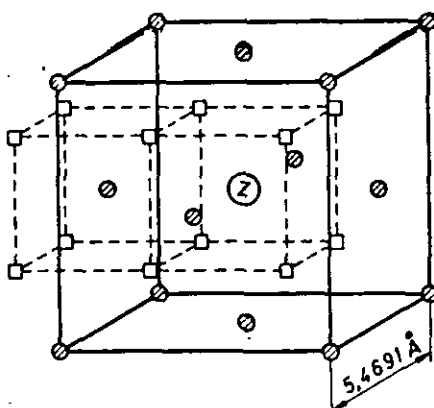


Fig. 2: Unit cell of UO_2 , \odot U-atom, \square O-atom, Z excess oxygen.

When UO_2 is oxidised, oxygen is taken up in interstitial positions to form the UO_{2+x} phase which has the same space group as that for stoichiometric UO_2 .

Uranium dioxide is generally made by adopting the following major steps: preparation of the starting material which can be uranyl nitrate⁽⁹⁾ or ammonium diuranate⁽¹⁰⁾ (ADU) or ammonium uranyl carbonate⁽¹¹⁾ (AUC), calcination of this at about $500^\circ \pm 50^\circ\text{C}$ to the oxide UO_3 , and finally reduction of UO_3 at $650 - 800^\circ\text{C}$ to UO_2 . Since the UO_2 powder is not thermodynamically stable in contact with oxygen, it is readily oxidised. Powders with high specific surface area ($> 10 \text{ m}^2/\text{g}$) may be either pyrophoric or at least oxidised rapidly at room temperature to U_3O_8 , while powders with a low specific surface area ($< 5 \text{ m}^2/\text{g}$) are not oxidized to U_3O_8 , but to an oxide with an O/U ratio according to the value of the specific surface area.

For the fabrication of sintered UO_2 pellets, conventional techniques, such as cold pressing and sintering to high densities of more than 95% of theoretical ($\text{TD} = 10.96 \text{ g/cm}^3$) can be applied.

As a nuclear fuel, uranium dioxide must be a high-density material which is close to the stoichiometric composition. This is not only to obtain a high uranium concentration in the reactor core, but also because the physical properties of the oxides, in particular its thermal conductivity is lower, its thermal expansion is larger and the fission gas release upon irradiation is more harmful, when densities are lower and the O/U ratios higher than the theoretical values⁽¹²⁾. In addition, UO_2 having a higher O/U ratio is less resistant to corrosion by high temperature pressurized water. Non-stoichiometry also exhibits an effect on the creep behaviour of uranium dioxide⁽¹³⁾. Diffusional or Nabarro-Herring creep

of uranium dioxide⁽¹⁴⁾ is affected by changes in stoichiometry through the influence of this variable on both diffusivity and on the ability of grain boundaries to act as sinks and sources for vacancies. It has been found that increasing the O/U ratio increases the creep rate at a fixed temperature and stress level. From the previously mentioned discussions, the O/U ratio of UO_2 used as a nuclear fuel was generally required to be no greater than 2.015⁽¹⁵⁾.

3. Experimental Methods of O/U Ratio Determination:

There are different methods for the determination of the O/U ratio, which of destructive or nondestructive characters. The destructive techniques used for the determination of O/U ratio include: (a) Gravimetric method⁽¹⁶⁻¹⁸⁾, (b) Chemical methods in which the oxide is dissolved in acid (HNO_3 or H_3PO_4) and then U (IV), U(VI) and total U content will be determined. Individual determinations are performed polarographically⁽¹⁹⁻²²⁾ titrimetrically⁽²⁰⁾, coulometrically⁽²¹⁾ or spectrophotometrically⁽²²⁾. As non destructive techniques: a) the measurement of electromotive force of a Ni-NiO, electrolyte - UO_{2+x} cell⁽²³⁾, b) X-ray diffraction⁽²⁴⁾.

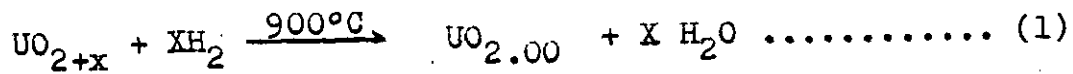
3.1. Destructive Techniques

3.1.1. Gravimetric Method:

This is the most important and abundant method of the destructive techniques. This method, according to the ASTM C 696-80, is applicable for UO_2 powder or sintered pellets in the range from UO_2 to UO_3 . The sample is converted to U_3O_8 by ignition and calculating the O/U ratio on the basis of weight change. The weight of U_3O_8 is corrected for the nonvolatile impurities present as determined by spectrographic analysis. The moisture content of the UO_2

(1000 - 3000 ppm) is taken into consideration too.

The O/U ratio can be obtained by using a direct reduction with hydrogen according to the following equation:



and measuring the water formed by absorption on anhydrous magnesium perchlorate⁽¹⁵⁾ or using a moisture analyzer based upon the electrolytic coulometric principle⁽¹⁶⁾.

In view of the preceding observations it will be clear that a knowledge of the behaviour of uranium in various oxidation states towards heating in oxidizing or reducing or inert atmosphere, is required. Fig. 3 shows the effect of these factors on the pure oxides and also on the metal⁽¹⁷⁾.

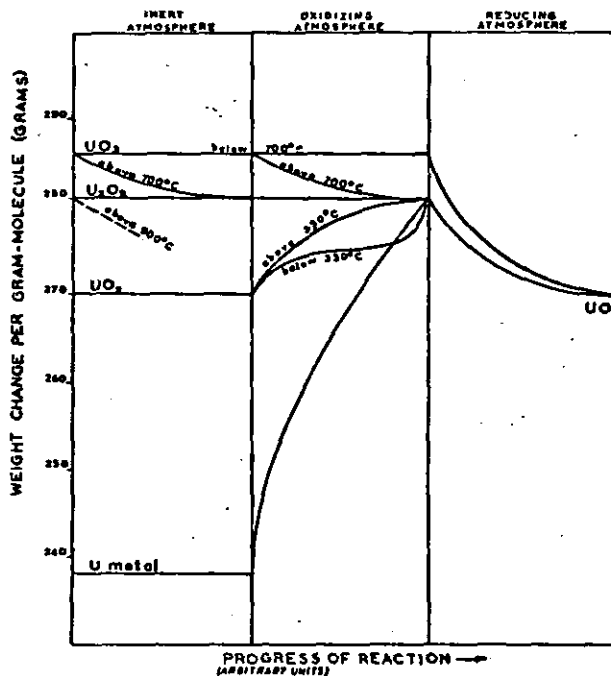


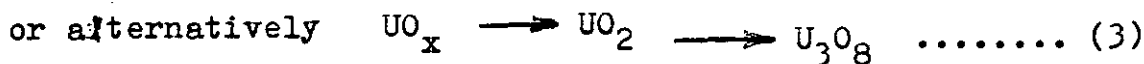
Fig. 3: Behavior of uranium and its principal oxides in various environments (temperature approximate)

The experimental observations on which Fig. 3 is based, can be summarised as follows:

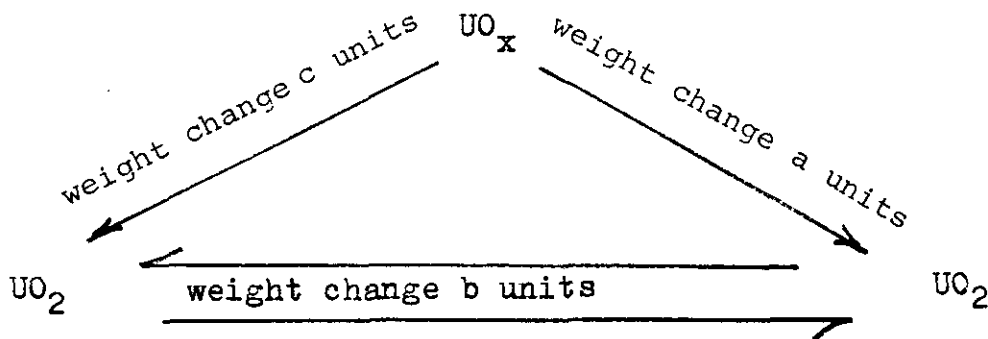
a) for complete conversion of the uranium of any mixture to pure U_3O_8 , it should be heated to $800^\circ C$ to constant weight in air to ensure decomposition of UO_3 , then cooled somewhat to compensate for a tendency of U_3O_8 to lose oxygen at that temperature.

b) for similarly complete reduction to UO_2 , the temperature is not a critical factor but can be chosen so as to give a suitable reaction velocity.

c) to ensure decomposition of hydrates, particularly of UO_3 , preliminary heating to at least $550^\circ C$ is advisable. The principle of the calculations required for the gravimetric method can be briefly discussed as follows: suppose that the conversion of the sample as UO_x can be considered according to the following reactions to an appropriate stoichiometric compound, either UO_2 or U_3O_8 , thus



The weight changes accompanying these reactions can be obtained directly from the thermogravimetric record. For any given weight of uranium, let these weights be a, b and c as shown diagrammatically:



The weight change in each reaction step will be proportional to the amount of uranium taking part (proportional constant K) and the change in its level of oxidation: therefore, for conversion UO_x to U_3O_8 to UO_2 :

$$a = K \left(2 \frac{2}{3} - x \right)$$

$$b = K \left(2 \frac{2}{3} - 2 \right)$$

$$\text{therefore } a/b = \left(2 \frac{2}{3} - x \right) / \frac{2}{3} = 4 - (3x/2) \dots\dots\dots (4)$$

Similarly for the alternative route UO_x to UO_2 to U_3O_8 :

$$c = K (x - 2)$$

$$\text{therefore } c/b = (3x/2 - 3) \dots\dots\dots (5)$$

Obviously the value of x is obtainable from either of these reaction cycles independently of the actual sample weight employed.

The gravimetric method can be described as follows:

Apparatus required:

- Analytical balance having a resolution of 0.1 mg
- Platinum crucible, 10 ml capacity diameter and height minimum 2.5 cm
- Muffle furnace capable of maintaining 1000°C
- Desiccator.

Sample Preparation:

Powder samples are used without any pretreatment. For samples received as sintered pellets, they must be cracked into small pieces.

Procedure:

- A sample of 5-10 g UO_2 powder or pellet material is weighed in the platinum crucible to the nearest 0.01 mg.

- The sample is heated at $470 \pm 25^\circ\text{C}$ for two hours and then fired at $900 \pm 25^\circ\text{C}$ for another two hours.
- The crucible is cooled in a desiccator to the room temperature, the weight of U_3O_8 is determined to the nearest 0.1 mg.

Calculations

For calculating the O/U ratio of UO_2 powder, the moisture content of the powder must be taken into consideration. For pellets, this is unimportant because the moisture content must not exceed 10 ppm H_2O

$$\text{O/U} = \frac{\text{dry weight of sample } W_d(\text{UO}_{2+x})}{\text{weight of ignited sample } W_i(\text{U}_3\text{O}_8)} \times 17.54168 - 14.8749 \quad \dots (6)$$

Example of calculation

$$\begin{aligned} \text{weight of crucible + sample} &= 38.4853 \text{ g} \\ \text{weight of crucible} &= 24.1830 \text{ g} \\ \text{weight of sample} &= 14.3023 \text{ g } (\text{UO}_{2+x} + \text{H}_2\text{O}) \end{aligned}$$

the moisture content of the sample for example 3000 ppm, the dry weight of the sample =

$$\begin{aligned} &= 14.3023 - 14.3023 \times 0.0003 = \\ &= 14.3023 - 0.0429 = 14.2594 \text{ g } (\text{UO}_{2+x}) \end{aligned}$$

After ignition to U_3O_8 :

$$\begin{aligned} \text{weight of crucible + } \text{U}_3\text{O}_8 &= 38.8990 \text{ g} \\ \text{weight of crucible} &= 24.1830 \text{ g} \\ \text{weight of } \text{U}_3\text{O}_8 (W_i) &= 14.7160 \text{ g } (\text{UO}_3) \end{aligned}$$

using equation (6)

$$\text{O/U} = \frac{14.2594}{14.7160} \times 17.54168 - 14.87499 = 2.122$$

3.1.2. Polarographic method:

This method covers the determination of oxygen to uranium atomic ratio in nuclear-grade uranium dioxide pellets when the ratio is between 2.00 and 2.10.

Apparatus required:

- Polarograph, with the necessary accessory equipment, capable of operating in the range from 0.2 to 5 uA.
- Kjeldahl dissolver flask, 100 ml equipped with a joint and a delivery tube for introduction of argon. A glas-Col type heating mantle, controlled by an autotransformer, is used to heat the flask.

Reagents

- Argon, oxygen-free
Nitrogen, helium or carbon dioxide containing less than 20 ppm oxygen may be substituted for argon.
- Perchloric acid (0.2 M) - dilute 17 ml of perchloric acid (HClO_4 , 72%) to 1 litre with water.
- O-phosphoric acid (H_3PO_4 , 85%)
- Uranium standard solution (1 ml = 1.00 mg U) dissolve 0.1179 g of uranium oxide (U_3O_8) (National Bureau of Standards NBS No. 95 a) in 2 ml of nitric acid (HNO_3). Add 5 ml of sulphuric acid (H_2SO_4) heat to fumes, cool and dilute to 100 ml with water.

Preparation of Calibration Curves

- Deliver 40 ml of H_3PO_4 and 50 ml of 0.2 M HClO_4 into each of eight 100 ml volumetric flask.
- Transfer 0.200, 0.400, 0.800, 1.00, 2.00, 4.00, 8.00 and 10.00 ml of uranium solution (1 ml = 1.00 mg U) successively to the eight flasks and dilute each to volume with water.

- Record a polarogram on each standard solution at all possible sensitive, scanning from ± 0.1 V versus the saturated calomel electrode (SCE) to more negative potentials, until a good diffusion current plateau is obtained. Plot the wave height versus uranium (VI) concentration for each sensitivity.

Procedure:

- Transfer a weighed portion (100 to 200 mg) of the uranium dioxide sample to the kjeldahl dissolver flask.
[pellets of uranium dioxide must be crushed and cooled in an inert atmosphere before the test portion is weighed. Exclude granules that are less than 1 mm on edge or less than 10 mg pieces.]
- Cover the weighed oxide with 40 ml of H_3PO_4 and bubble argon through the solution at a rate of 1 to 2 bubbles per second.
- Turn on the heating mantle and adjust the autotransformer to heat the solution to near boiling.
- When the oxide is completely dissolved turn off the autotransformer and remove the heating mantle .
- Bubble argon through 50 ml of 0.2 M $HClO_4$ at a rapid rate for 10 min. Add this solution to the dissolver flask in three portions while increasing the gas flow through the H_3PO_4 to provide mixing. Add successive portions of the 0.2 M $HClO_4$ solution only after any cloudiness has cleared.
- Cool the solution to room temperature and dilute it to 100 ml with water. Bubble argon through the solution to ensure mixing.
- Transfer a portion of the solution to the polarographic cell, deaerate for 1 min. and record the polarograms at the

- highest sensitivity to obtain the U(VI) reduction wave at - 0.17 V versus SCE.
- Determine the U(VI) concentration by reference to the appropriate calibration curve.

Calculation of O/U Atomic Ratio:

- Calculate A, the provisional atom fraction of excess oxygen, as follows:

$$A = 100 C / 1000 W (0.8815)$$

where:

C = concentration of U(VI) determined, $\mu\text{g/ml}$

W = weight of sample taken, mg

0.8815 = fraction of U in stoichiometric uranium dioxide of natural abundance

100 = volume of solution ml, and

1000 = factor of changing micrograms to milligrams.

- Calculate A_c , the corrected atom fraction of excess oxygen as follows:

$$A_c = A \left[1 + (0.1) A \right]$$

- Calculate the mole ratio of oxygen to uranium in the uranium dioxide sample as follows:

$$\text{Mole ratio, \%} = 2.00 + A_c$$

3.1.3. Titrimetric Methods:

The O/U ratio in uranium oxides has been determined by several titrimetric methods:

- (a) Dissolution in phosphoric acid and then titration of the sample solution by ceric sulphate or standard potassium dichromate⁽⁵⁾.

- (b) Dissolution in 1.5 N H_2SO_4 + Ce(IV) sulphate. Excess Ce(IV) sulphate is back titrated with Fe SO_4 using ferrion indicator^(21,23).
- (c) Dissolution in H_2SO_4 and direct titration by Fe SO_4 or Ti(III)⁽²⁷⁾.

An improved and simplified method was proposed by Dharwadker⁽²⁸⁾ which is generally suitable for O/U ratio determination unless a deviation less than ± 0.002 in O/U is required. This method is used at Bhabha Atomic Research Centre, India.

Reagents:

- Cerium (IV) sulphate
- Iron (II) ammonium sulphate
- Sulphuric acid
- 0.025 M ferrion indicator solution

Procedure:

The uranium oxide sample (50 - 175 mg) is weighed and dissolved directly in a known excess of 0.1 M cerium (IV) sulphate solution in 3N sulphuric acid. The dissolution is quite rapid at 70°C. Sufficient 5N sulphuric acid must be added to make the solution 3N in sulphuric acid at the equivalence point, and the excess of cerium (IV) present in when titrated with a freshly prepared standard iron(II) ammonium sulphate solution using ferrion as indicator. The cerium (IV) solution must be standardized just before analysis and prepared by dissolving pure cerium (IV) sulphate in 5N sulphuric acid and diluting to give a 3N acid solution.

A precision of ± 0.003 in O/U ratio can be obtained for samples of $\text{UO}_{2.02}$ to U_3O_8 . For samples with O/U ratio above

about 2.05, the determination of uranium (IV) can give more precise results than the polarographic method.

3.1.4. Spectrophotometric Method:

In this method the sample is dissolved in hot concentrated phosphoric acid and the concentration of U(IV) and U(VI) are measured via the absorbance of two specific wave lengths. This method is simple and requires little time. It has been tested for O/U ratio between 2.05 and 2.62. The reproducibility, related to the O/U ratio is $\pm 0.005^{(29)}$. This method is now applied in Nukem West Germany.

Requirements:

- Conc. phosphoric acid
- spectrophotometer
- Hot plate

Procedure:

1- Dissolution of the UO_2 samples

- Transfer a weighed portion (200 mg) of the sample to a preheated dissolver flask.
- Add 10 ml of hot conc. H_3PO_4 and heat the flask gently. To avoid the oxidation of the sample with air, dissolution must be carried out under inert gas. Time of dissolution is 1.2 minutes at $130^\circ C$.
- Cool the solution to room temperature.

2- Measure the absorbance at two specific wave lengths of 544, 516 and 420

$$\text{Using } A_{544} = A_1 \text{ (for U(IV))} \dots \dots \dots (7)$$

$$A_{516} = A_2 \text{ (used as datum punk)}$$

$$A_{420} = A_3 \text{ (for U VI)} \dots \dots \dots (8)$$

Fig. 4 shows the uranium spectra in conc. H_3PO_4

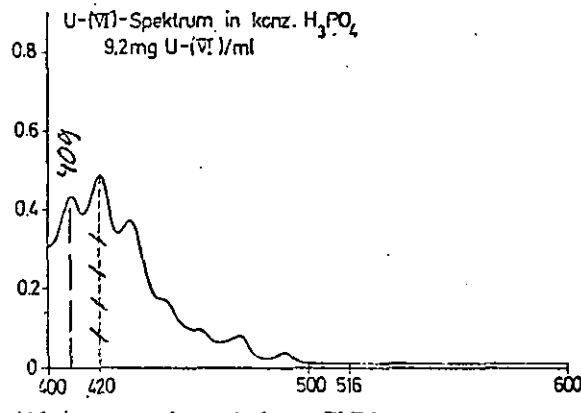
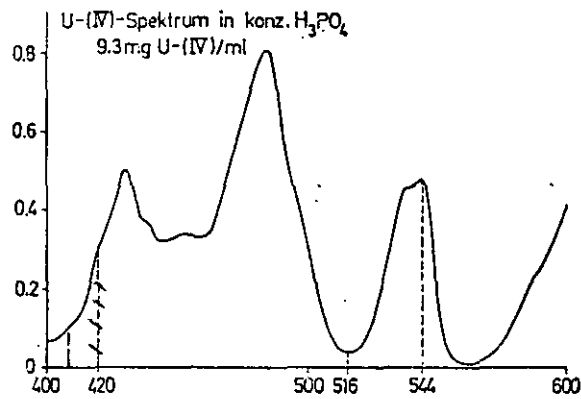


Fig. 4: Uranium spectra in conc. H_3PO_4 .

Calculations:

The concentration of U(IV) is calculated according to the following equation:

$$C_{U(IV)} = 21.066 (A_1 - A_2) \dots\dots\dots (9)$$

By consideration the accompanied U(IV) with U(VI) at wave length 420, then

$$A_{U(IV),420} = 0.02418 C_{U(IV)} \dots\dots\dots (10).$$

The concentration of U(VI) is then calculated as follows:

$$C_{U(VI)} = 19.395 (A_3 - A_2 - A_{U+V,420}) \dots\dots\dots (11).$$

The O/U ratio can be obtained from the following relation:

$$O/U = 2.C_{U(IV)} + 3.C_{U(VI)} / (C_{U(IV)} + C_{U(VI)}) \dots\dots (12)$$

The reproducibility of this method, related to the O/U ratio, is ± 0.005 in the range of 2.05 to 2.67.

3.1.5. Infra-red Spectroscopy Method:

The infra-red (IR) spectra ($200 - 1000 \text{ cm}^{-1}$) of UO_{2+x} ($x = 0.002 - 0.1153$) were investigated⁽³⁶⁾. The dependence of the ratio of absorbances of the transverse and longitudinal optical branches TO, LO respectively of the IR-active T_{LU} band at $250 - 500 \text{ cm}^{-1}$ on the O/U ratios was constructed. This method is rapid for quantitative determination of O/U ratio with a range of 2.000 - 2.110 with precision ± 0.004 O/U units.

Apparatus required:

- IR-spectrometer
- Potentiometer for titration
- Motor for sample grinding

Reagents:

Conc. H_3PO_4

Procedure:

1- Preparation of calibration curves:

- Samples of UO_{2+x} with predetermined x were used as

standards for measuring the dependence of the TO/LO absorbance ratio on the O/U ratios. The samples must be in finely divided form.

- The IR spectra of the standards will be measured within the ranges of 200 - 1000 cm^{-1} .
- The IR spectra obtained were evaluated by calculating the maximum absorbances on the TO ($\sim 330 \text{ cm}^{-1}$) and LO ($\sim 460 \text{ cm}^{-1}$) branches of the UO_{2+x} absorption band and determining their ratio (TO/LO).

The IR spectra of the UO_{2+x} standards, possessing the x values of 0.002 and 0.1155 are given in fig. 5. The values of the TO/LO ratio obtained for individual standards is shown in Fig. 6.

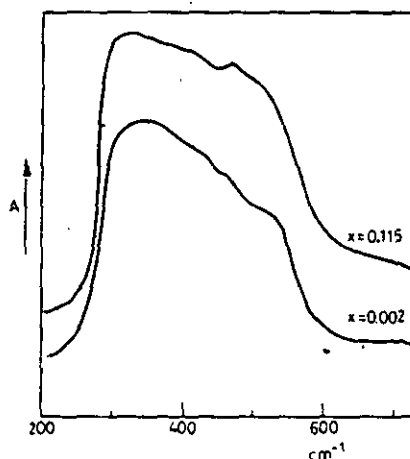


Fig. 5: The IR spectra of the UO_{2+x} standards with given x values.

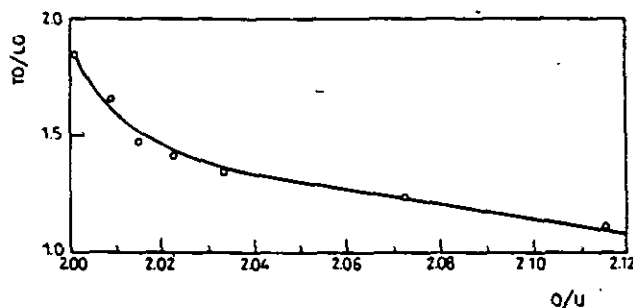


Fig. 6: The dependence of the TO/LO ratio on the O/U ratio.

3.1.6. Coulometric Method:

This method covers the determination of the oxygen to uranium ratios above 2.01, it gives more precise results than the polarographic procedure, but conversely would be less applicable to near stoichiometric material.

The method is based upon a controlled potential coulometric titration of uranium (VI) and total uranium of the oxide sample after dissolution in hot concentrated phosphoric acid in the absence of oxygen. The fraction of uranium (VI) in the uranium oxide is directly related to the oxygen to uranium ratio.

Apparatus:

- A controlled potential coulometer using computer amplifiers to control the titration potential and integrate the cell current.
- Two Philbrick plug-in amplifier; one for potential control and the second for current integration.

- Dissolution apparatus: Plattner's Diamond mortar and pestle are used to crush the samples. A 100-ml. volumetric flask is used as the dissolution vessel. The flask is fitted with a stopper with inlet and exit tubes to accommodate an inert gas sweep.

- Electrolysis cell:

Reagents:

- Phosphoric acid
- Helium gas
- Sulphuric acid
- Ceric sulphate

— Accuracy 1% standard deviation.

Procedure:

About 0.5 gram sample of the oxide which has been previously crushed, if necessary is placed in the flask with 20 ml of deoxygenated 85% phosphoric acid. Helium is passed over the mixture to prevent air oxidation of the sample and the flask is placed on the hot plate set at its maximum temperature. After the dissolution is complete and the solution is cool, 80 ml. of de-oxygenated 1 M sulfuric acid is added to the solution, and the solution is diluted to 100 ml. with deoxygenated distilled water. During the dilution, a gelatinous precipitate may form, but will redissolve when the solution is stirred. One ml. of the solution is added to 10 ml. of 1 M sulfuric acid in the electrolysis cell. The sample volume is chosen so that the total uranium titrated will correspond to full-scale on the least sensitive integrator range. After selection of the proper integrator range for the sample, the sample is prereduced at + 0.05 volt versus S.C.E. This last reduction, corrected for the blank, gives uranium (VI) content (The blank

is determined by following procedure with no uranium added, and corresponds to 5 μ g of uranium). Twice the amount of ceric sulfate (reagent grade) necessary to oxidise the uranium to uranium(VI) is added to the solution in the electrolysis cell. After 3 minutes has elapsed the sample is prerduced (to remove excess ceric ion) and reduced as before. This reduction corrected for the blank, gives the total uranium, and the O/U ratio can be calculated from the equation, $O/U = 2.000 + U(VI)/U$. The total time for the described titration is about 35 minutes.

3.2. Nondestructive Techniques:

3.2.1. X-ray diffraction method:

According to X-ray diffraction studies of uranium oxides in the $UO_2 - U_4O_9$ region a relation has been found between the lattice constant and the O/U ratio, as shown in Fig. 7

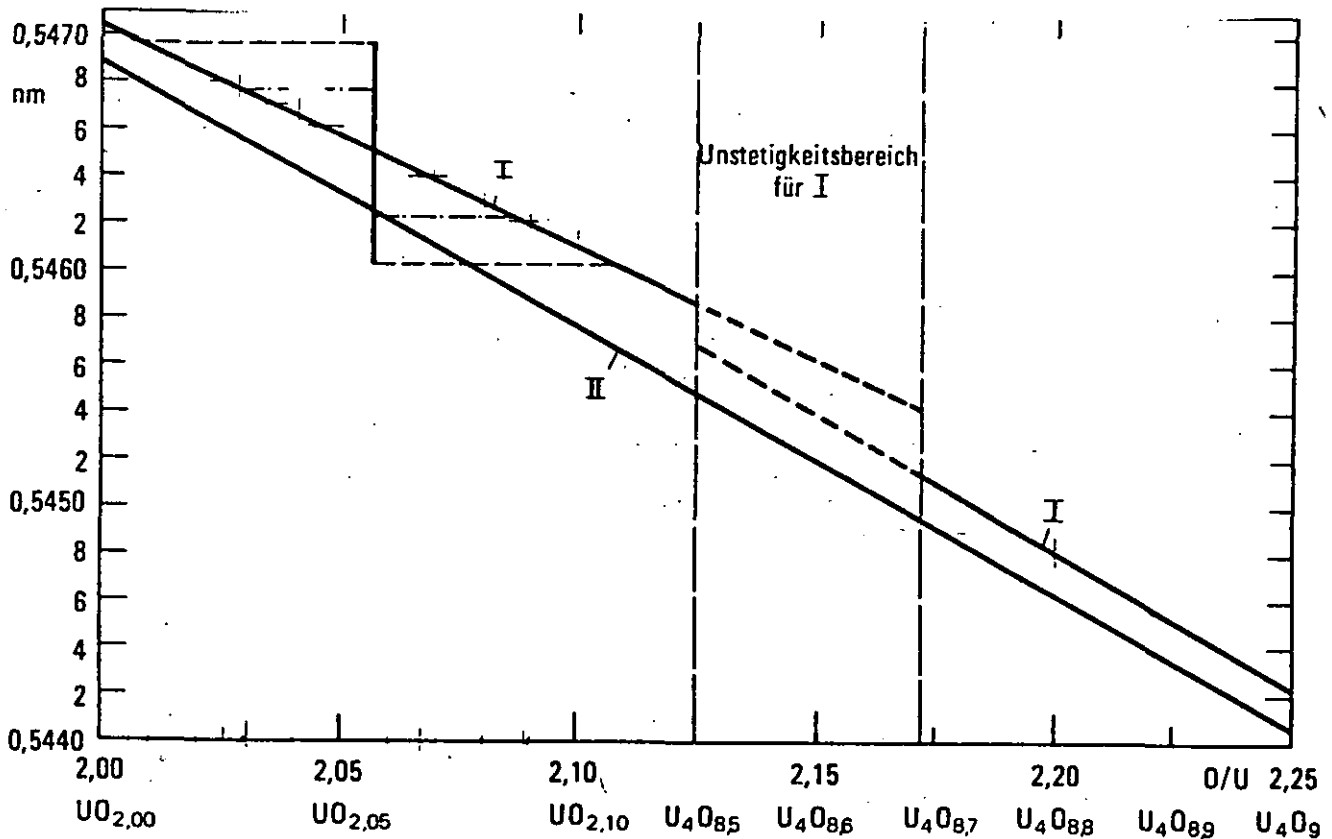


Fig. 7 The relationship between the lattice constant & the O/U ratio.

For the determination of the lattice constant, line broadening of the X-ray powder diffraction is used within the application of the Bragg equation:

$$\lambda = 2 d_{(hkl)} \sin \Theta \dots\dots\dots (13).$$

where:

λ = wave length

d = distance between two atomic layers

Θ = the reflection angle

h, k, l = constants describing crystallographic planes.

From equation (13) d can be calculated as follows:

$$d_{(h, k, l)} = \frac{\lambda}{2 \sin \Theta} \dots\dots\dots (14).$$

From ASTM-cards for X-ray investigation results of $UO_2 - U_4O_9$ system, the constants h, k, l are taken. The relation between the lattice constant (a) and the h, k, l constants is:

$$d_{(h, k, l)} = \frac{a}{(h^2 + k^2 + l^2)^{1/2}} \dots\dots\dots (15).$$

From equations (14) and (15):

$$a = \frac{2 \sin \Theta}{\lambda} (h^2 + k^2 + l^2)^{1/2} \dots\dots\dots (16).$$

For example, by using $Cu K_{\alpha}$ radiation

$$\begin{aligned} \lambda &= 1.5405 \text{ \AA} \\ 2\Theta &= 87.42^\circ \end{aligned}$$

it follows from equation (14): $d = 1.1147$

From the ASTM-cards:

$$hkl = 422 \longrightarrow h = 4 \quad k = 2 \quad l = 2$$

and by using equation (16): $a = 5.4608 \text{ \AA} = 0.54608 \text{ nm}$.

By calculation of the mean value of a (for example $= 5.4610 \text{ \AA}$)

and using the Fig. (7), an O/U ratio of 2.07 obtained.

3.2.2. High-temperature galvanic cell method:

The most promising non-destructive method appears to be the determination of the emf, which increases with increasing O/U ratio. It is determined with the aid of high temperature galvanic cells.

Electromotive force measurements on galvanic cells involving solid electrolytes have been made at temperatures of 700 - 1200°C in order to obtain standard thermodynamic data for the mixing of UO_2 and oxygen gas^(31,32). Due to the purely anionic conductivity of the electrolyte, a direct evaluation of the partial pressure of oxygen in uranium oxide as a function of the O/U ratio and temperature has been possible shown in Fig. 8, 9.⁽²³⁾

The most commonly used electrolyte for oxygen concentration cell is zirconia stabilized with calcia^(23,33,34). Pure ZrO_2 crystallizes in a monoclinic ($T < 1200^\circ C$), tetragonal ($1200 < T < 2200^\circ C$) and cubic structure ($T > 2200^\circ C$), but addition of CaO from 12.5 to 22.5 mole% the cubic form can be stabilized to low temperatures. The non-stabilized structures show both ionic and electronic conductivity, whereas the stabilized cubic ZrO_2 -CaO solid solutions show predominately ionic conductivity within certain oxygen pressure ranges, which makes these oxides especially suitable for oxygen concentration cells. A cell of the NC, NCO) $ZrO_2(CaO) \mid UO_{2+x}$ type was usually used.⁽³⁵⁾

The principle of the cell is shown schematically in Fig. 10.

The cell is constructed from a zirconia tube stabilized with CaO. Porous platinum electrodes are applied inside and

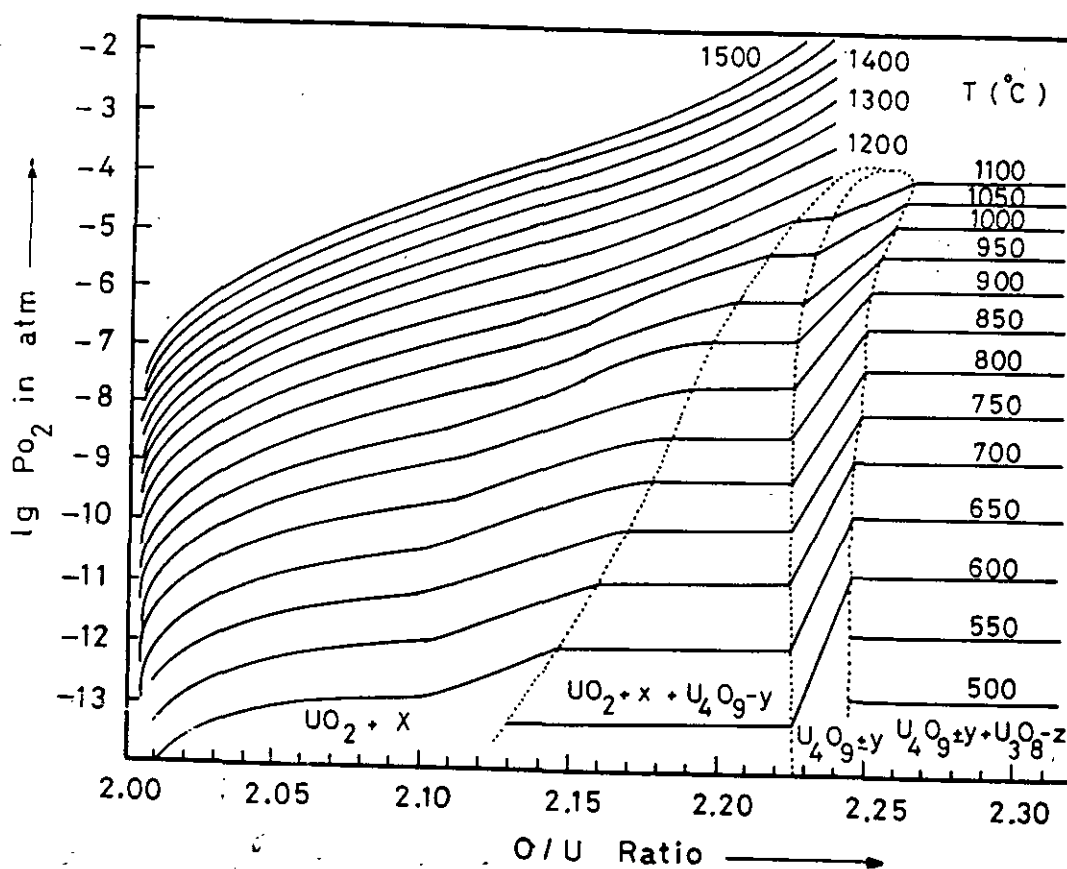


Fig.8. Partial pressure of O_2 versus o/u ratio outside the closed end of the tube and on an outside track along the tube by painting with platinum paste and firing in air at about $1000^{\circ}C$ for about 5 hours using a heating and cooling rate of $100^{\circ}C/h$ to avoid cracking the tube. After the first firing the electrode at the closed end of the tube appeared to be bright and to have good adherence contact to the internal platinum electrode is obtained with a platinum wire welded to a thin platinum disk that is pressed against the electrode with an aluminium support tube. A four-bore thermocouple protection tube placed inside this tube contained the contact wire as well as a Pt/Pt,Rh(10%) thermocouple. With flanges fastend gas-tight to the ZrO_2 -tube and to the support tube, the reference gas (air) supplied to the internal electrode through the support tube and then leave the system through the space between the ZrO_2 -tube and the support tube.

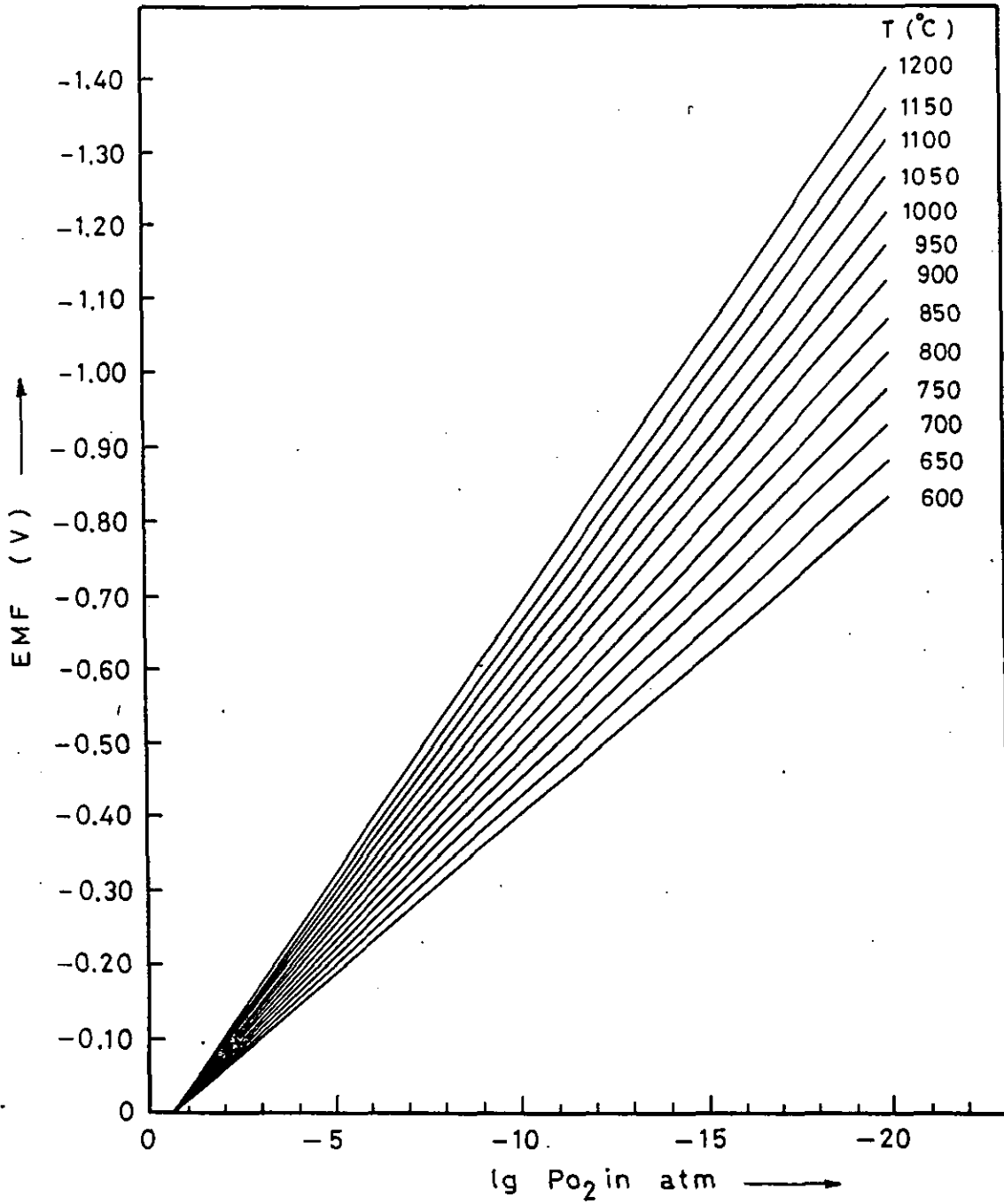


Fig.9 Partial pressure of oxygen versus e.m.f.

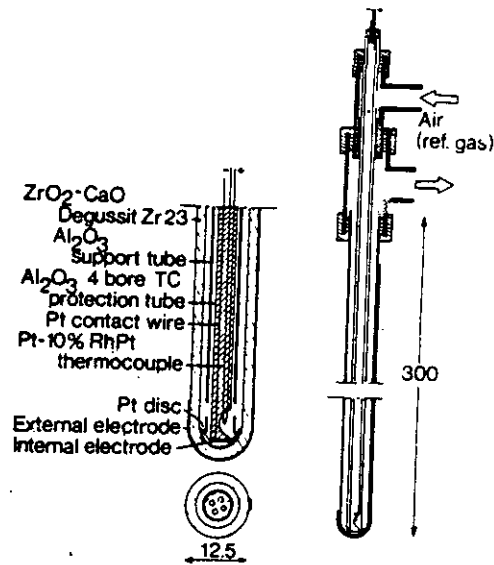


Fig. 10 Principle of ZrO₂ (CaO) cell.

High temperature galvanic cells have the advantage over other methods of O/U determination that the sample is not destroyed and essentially unchanged, so that further studies on it, e.g., neutron diffraction, can be carried out. Once the necessary equipment has been established the method is rapid, and a precision of ± 0.002 O/U units can be obtained. Agreement between the emf method and destructive methods is excellent, which make it the most promising non-destructive method for O/U determinations.

4. Summary

Table 1 lists the analytical procedures which can be employed for the determination of O/U ratio in UO₂.

Table 1

Methods	Sample preparation	Determination procedure	O/U ratio-accuracy	Remarks
<u>Destructive Methods:</u>				
1. Thermo Gravi- metric methods	5 gm sample weighed out	weighed sample heated at 470°C for 4 hrs, then at 900°C for 4 hrs and weighed	± 0.002	Standard (ASTM-C696)
2. Polarographic methods	Dissolution of sample in H_3PO_4	U(VI) reduced to U(IV), polarographic determination of U(VI), potentiometric determination of U(IV) by $K_2Cr_2O_7$	± 0.015	Standard
3. Titrimetric methods	Dissolution in H_3PO_4 or dissolution in 1,5 N H_2SO_4 + Ce(IV) sulphite	Titration of sample sol. by ceric sulphate or dichromate Backtitration by $FeSO_4$ & ferroin indicator	± 0.003	applied in W. Germany (Nukem) & India
4. Spectrophotometric method	Dissolution in hot conc. H_3PO_4	Measurement the concentrations of U^{4+} & U^{6+} via the absorbance of two specific wave lengths (544, 420).	± 0.005	Used in Germany (Nukem)
5. Infrared spectroscopy	Dissolution in H_3PO_4	Measurement the infrared spectra (200-1000 cm^{-1})	± 0.004	

6. Coulometric method
 Dissolution in $H_3PO_4 + H_2SO_4$
 Reduction of U(VI) component at constant voltage. Oxidation of total U by conc. sulphate and reduction to U(IV) ± 0.0003

Non destructive

Methods:

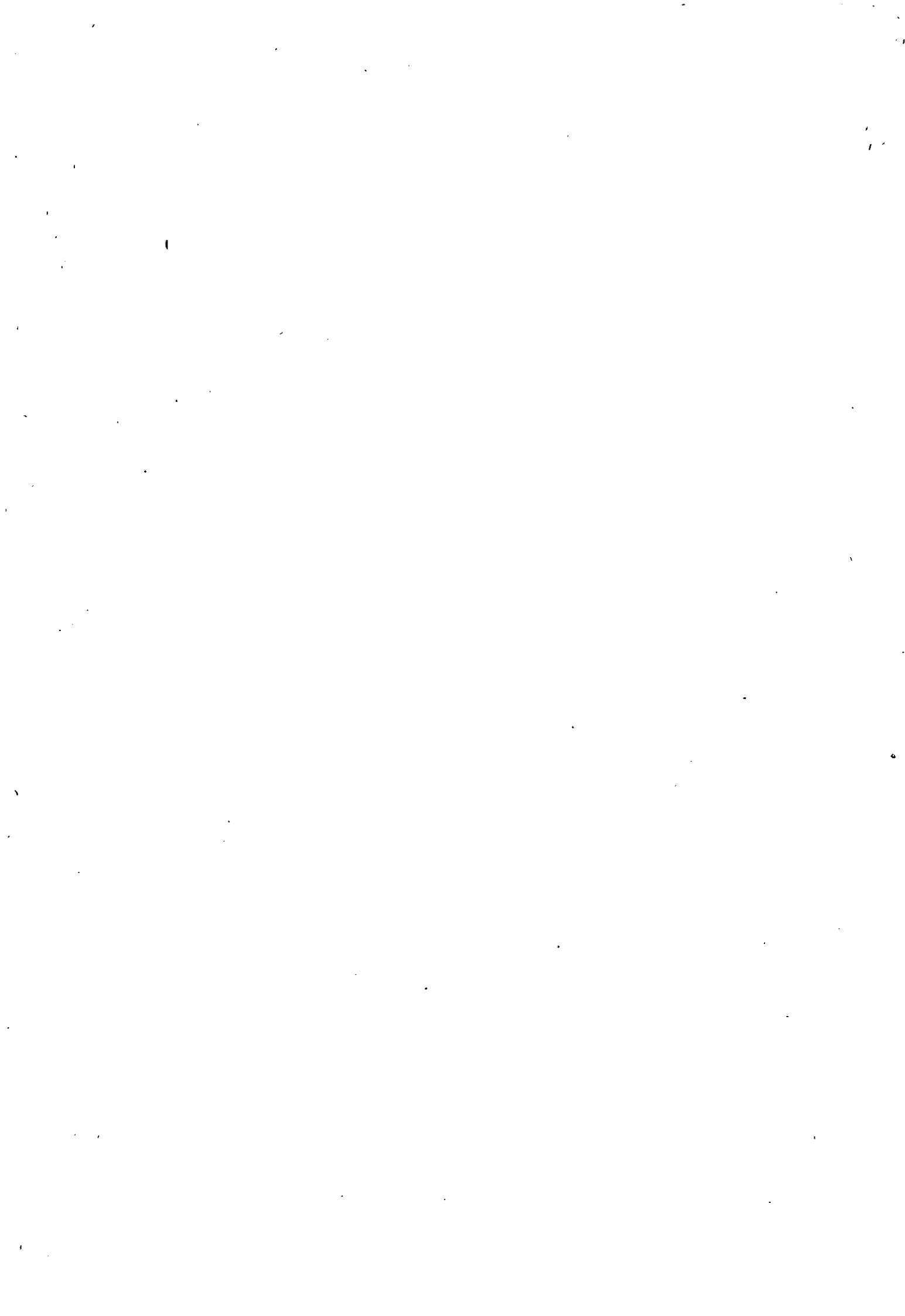
1. X-ray diffraction	Powder form	Determination the lattice parameter which dependent on the O/U ratio	± 0.005	applied in W. Germany KWU-Nuclear fuel laboratories
2. High temperature galvanic cells	Pellets	Construction of galvanic cell Ni, NiO/ZrO ₂ , CaO/UO ₂ +x; heating to 700-1100°C and measurement of emf	± 0.002	

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