

FUEL CHARACTERIZATION TECHNIQUES: CURRENT METHODS PRACTISED AT THE INSTITUTO DE PESQUISAS ENERGÉTICAS E NUCLEARES, BRAZIL

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The paper outlines the present status of fuel characterization methods which are practised at the Instituto de Pesquisas Energéticas e Nucleares, IPEN, Brazil, to be applied in the field of process and product control of oxide powder and pellets for reactor application.

The main fuel characteristics usually determined in product and process control of UO_2 powders and pellets are chemical, physical, isotope enrichment, geometrical and microstructural.

Instrumental, wet chemical and physical laboratories have been set up to provide the adequate attendance to the above necessities. The main characterization methods established in these laboratories are described.

1. Introduction

Achievement of high quality standard in the design and development of nuclear fuel assemblies requires special manufacturing techniques as well as rigorous testing procedures of fuel components.

For a particular manufacturing route, special procedures of process control and product control are required. These procedures are established according to the specific manufacturing route and the control plans are scheduled for monitoring the main fuel characteristics.

The important fuel characteristics usually determined in product and process control of UO_2 powders and pellets are isotope enrichment, chemical, physical, geometrical and microstructural.

The Instituto de Pesquisas Energéticas e Nucleares – IPEN is presently engaged in organizing quality control and quality assurance activities for PWR fuel production. As a part of these activities, various characterization Techniques have been developed to be employed in the fuel oxides controls. These techniques are related to the measurements of the uranium isotopic ratio, the chemical properties and the physical properties of uranium oxides powders and pellets, under the general scheme of product and process controls.

2. Isotope analysis

Isotope analysis of uranium samples are carried out using a double filament assembly in a Varian TH5 thermionic mass spectrometer, which has been automated for

data acquisition and processing using a locally available microcomputer system [1]. The sample is deposited in the form of nitrate on one side of the filament made of zone refined rhenium, using a programmable sample dryer unit, similar to that developed by Gramlich and Schideler [2]; samples are evaporated and this allows reproducible automatic loading of the samples. Although we have carried out single filament thermionic emission experiments using reducing agents to improve the emission of U^+ ions [3], our experience shows that use of double filament assembly is most adequate for precise routine analysis. The ion detection is carried out using Faraday cup and though larger amount of sample loadings are necessary ($\sim 5 \mu\text{g}$), the advantage lies in the fact that the mass discrimination induced by the detector is practically eliminated.

The data acquisition consists in integrating four measurements on top of each peak with eight scans in each of the three runs. The data are processed and using statistical considerations the isotope ratios, atom percent and weight percent of individual runs, the mean and the standard deviation are printed.

The isotope measurements show that the internal precision is dependent on the value of the isotope ratio [4] and this observation has been confirmed by us in the course of our participation in the International programme on "Isotope Dilution Analysis-80 (IDA-80)". Based on many analysis in our laboratory, the internal precision for uranium isotope ratios nearer to the natural abundance, i.e. $^{235}\text{U}/^{238}\text{U} \sim 0.00727$, was found to be 0.3%.

To test the accuracy of our measurements, isotopic analysis are carried out in the NBS uranium isotopic

standards and the results show that the measured values are in agreement with the certified values [5]. NBS uranium isotope standard U500 is used to determine periodically the value of the mass discrimination factor.

3. Chemical methods

3.1. Determination of impurities

3.1.1. Spectrochemical procedures

In the atomic emission spectroscopy used for the determination of many elements at low concentrations in uranium matrix, the complex nature of the emission spectrum of uranium requires either the removal of uranium prior to excitation or the avoidance of uranium to enter in the arc region.

The commonly used direct method for determining the impurity elements in uranium based materials has been the carrier distillation [6–8]. Adequate detection limits for many impurities of nuclear interest, particularly those having large neutron-capture cross sections, can be obtained with any form of the carrier distillation technique.

The lanthanides are usually determined with previous concentration chemical procedures [9].

In the last few years, the inductively coupled plasma (ICP) has been accepted as new tool for routine trace impurities determinations in uranium compounds [10–13]; detection by ICP/mass spectrometry is also a new technique [14].

The group of elements called general impurities are routinely determined by carrier distillation technique. Twenty metallic impurities are determined with an imprecision lower than 15–20%. The experimental conditions, selected lines and concentration ranges [15,16] established in our spectrochemical laboratory are shown in table 1.

The Na, K and Li, whenever necessary, are determined through control by flame photometry [17]. The uranium is extracted with tri-n-butyl phosphate (TBP) in chloridric medium and the remaining aqueous phase is analysed by flame photometry. The relative standard deviation of the method is of the order of 10%. The relative errors vary with the concentration of the elements and range from 1 to 24% for Na, up to 12% for K and up to 33% for Li.

The elements Nb, Hf, Mo, Ta, Ti, V, W and Zr are determined as a separate group using a modified ASTM-C696 procedure [18]. The impurities are separated from an uranyl sulfate solution with previous addition of iron, by precipitation with cupferron followed by extraction of cupferrates with a mixture of isoamyl alcohol and chlo-

roform. The organic phase of extraction is evaporated, dried and calcined. The product is weighed and Fe_2O_3 is added up to 20 mg; graphite with 8% NaF and 200 $\mu\text{g/g}$ Pd (internal standard) is added to this mixture in a proportion of 1 : 1. Amounts of 10 mg of the last mixture are arced in a AGKSP-L4030 (National Carbon Co.) graphite electrode and the spectrum is recorded for a period of 75 s without pre-burn on SA-1 Kodak photographic plate. From the equivalent of 10 g U, the detection limits are 0.1 $\mu\text{g/g}$ Hf, 0.25 $\mu\text{g/g}$ Mo, 1 $\mu\text{g/g}$ Ta, 0.16 $\mu\text{g/g}$ Ti, 0.25 $\mu\text{g/g}$ V, 1.0 $\mu\text{g/g}$ W and 0.6 $\mu\text{g/g}$ Zr. The relative standard deviations fall in the range of 3.7 to 18%, except for Ta for which it is 37% [19].

The lanthanides are also determined as a separated group, after chemical separation of uranium. The uranyl nitrate solution with 0.3M HF is percolated in a small alumina column. The uranyl ion is not retained whereas the thorium and rare earths are adsorbed on the alumina. The elution of the rare earths is carried out with hot 1M HNO_3 ; 5 mg of La are added to the solution and the rare earths are co-precipitated as oxalates. After filtration, the oxides are ignited at 900° C for 1 h; the residue is mixed with the same amount of graphite powder. 10 mg of this mixture are excited for 60 s in a 17A DC under A-O₂ atmosphere. For the equivalent of 100 g U, the detection limits range from 0.001 to 0.05 $\mu\text{g/g}$ depending on the lanthanide [15,20].

3.1.2. X-ray fluorescence spectrometry

The X-ray fluorescence spectrometry has been applied in some branch of the nuclear fuel cycle [21–25].

The simultaneous determination of low concentration of Ca, Cr, Cu, Fe, Mn and Ni in uranium deoxides is performed using an X-ray fluorescence spectrometer, without the use of chemical treatment.

Standards are prepared by adding known amounts of Ca, Cr, Cu, Fe, Mn and Ni to an U_3O_8 matrix, which is chemically more stable than UO_2 and has a similar matrix behavior. Samples are prepared in the form of double-layer pellets with boric acid as a binding agent [26].

A tungsten target X-ray tube and a scintillation counter are used for Cr, Cu, Fe, Mn and Ni; a chromium tube and flow proportional counter are used for Ca. The analyser crystal is LiF (200) for all elements except Ca, for which an EDDT (020) crystal is used.

The sensitivities and estimated detection limits (3σ criterion) are given in table 2.

The imprecision and inaccuracy of the method are similar to those achieved with emission spectrometry [27].

3.1.3. Fluorine and chlorine

The fluorine and chlorine are usually determined with previous separations of halogenes from uranium oxides

Table 1

The experimental conditions, selected lines and concentration ranges for spectrochemical determinations of impurities in UO₂ powders and pellets

Experimental conditions	Carrier	Element	Wavelength (nm)	Concentration range (μg/g)
Jarrel-Ash 3.4m spectrograph	6% NaF	Si	215.432	260 – 6
590 lines per inch grating		Al	256.799	500 – 14
220–340 nm region		Mn	279.482	54 – 2
Voltage and current:		Mg	279.533	100 – 2
		Pb	283.306	50 – 1
230 V, 10 A, DC arc 8 A (for Ca)		Sn	283.999	50 – 1
		Bi	306.772	50 – 2
upper SPK-L 4236, lower AGKPS-9066 (National Carbon Co.) Electrodes 4 mm gap		V	318.341	100 – 3
		Cu	327.396	51 – 1.4
5 s and 10 s (for Ca) pre-burn		Ba	455.503	100 – 1
35 s and 60 s (for Ca) exposure	Co	340.512	100 – 10	
10 μm slit width	6% AgCl	Cd	228.802	5 – 0.1
120 mg (U ₃ O ₈ + carrier) charge		B	249.773	5.2 – 0.1
SA-1 Kodak emulsion		P	255.328	500 – 55
		Fe	259.837	520 – 14
		Ni	305.082	110 – 4
		Cr	284.325	95 – 5
		Mo	313.259	51 – 2
		Zn	334.502	500 – 10
	50% AgCl	Ca	393.367	25 – 2

Table 2

Sensitivity and lower limit of detection of impurities in uranium dioxide by X-ray fluorescence spectrometry

Element	Sensitivity (10 ³ counts/s/%)	Lower limit of detection (μg/g)
Ca	17.0	4
Cr	2.2	4
Cu	10.1	5
Fe	6.9	3
Mn	3.7	2
Ni	15.0	2

by the pyrohydrolysis at a temperature of 950–1100° C in a stream of wet oxygen and followed by spectral photometric or ion-selective electrode methods [18,28].

An alternative separation procedure consists in the use of a strong cationic resin to retain the uranyl ion. The fluorine and chlorine anions are determined in the effluent solution by selective electrodes; the detection limits are 0.02 μg F⁻/ml and 1.0 μg Cl⁻/ml [29]. Similar results are obtained by means of ion chromatography with previous pyrohydrolysis separation [30].

3.1.4. Hydrogen, nitrogen, carbon and sulfur

The contents of hydrogen, nitrogen, carbon and sulfur are determined by commercial equipments, in uranium oxide pellets, by hot extraction followed by chromatographic measurements. The hydrogen and nitrogen are determined with the instrument VH-9 (Leybold-Heraeus), and carbon and sulfur with the instrument CS-244 (LECO), which have enough sensitivities to perform specification control of UO₂ pellets, e.g. according to ASTM [31].

3.2. Total and absorbed gases

The quantitative and qualitative analysis of different gaseous components (excluding water vapour) occluded in sintered UO₂ pellets are performed in a high temperature vacuum extraction system coupled to a quadrupole mass spectrometer.

The high temperature gas extraction and analysis apparatus were designed and assembled for sequential analysis of up to four uranium dioxide pellets [32], according to ASTM [18] recommendation.

Quantitative and qualitative gas analysis are performed using a Varian quadrupole mass spectrometer. The sample introduction system connected to the mass spectrometer consists of a one litre glass expansion bulb cou-

pled to a cold trap, leak valve and a thermocouple gauge. The bulb can be evacuated and filled with gas at a desired pressure.

The variation in the quantity of the gases liberated from UO_2 pellets as a function of temperature shows that CO , N_2 and CO_2 are totally liberated at temperatures of 1000°C whereas the hydrogen is liberated above 1500°C and at 1700°C is the major component in the liberated gas mixture. Hence, the measurement of hydrogen is performed at a temperature of 1700°C [33].

3.3. Stoichiometry, uranium and water content

3.3.1. Titrimetric method

Uranium dioxide is dissolved in a mixture of 1:2 concentrated sulfuric acid and phosphoric acid. The U(IV) is determined in the cold solution, after addition of iron(III) chloride, by titration with 0.02N potassium dichromate and barium diphenylamine sulfonate used as indicators [34].

The total amount of uranium is determined by previous reduction of uranium(VI) to uranium(IV) in the presence of a known amount of iron(III), with tin(II) chloride; the excess of tin(II) ion is subsequently oxidized with mercury(II) chloride. From the content of uranium(VI), obtained by difference, the contents of uranium(VI) and total uranium, the O/U ratio are derived [35]. An improved titrimetric method for the determination of the O/U ratio in uranium oxide was developed by Khatoun and Rao [36], recently.

3.3.2. Gravimetric method

A weighed portion of UO_2 is dried in a nitrogen atmosphere and desiccated. The dried oxide is converted to U_2O_8 at 800°C for 3 h in an oxygen atmosphere. The uranium content is derived from the weight of U_3O_8 corrected for the non-volatile impurities determined by spectrographic analysis [15]; the oxygen to uranium ratio is also derived from the weight of U_3O_8 corrected for the non-volatile impurities determined by spectrographic analysis [15]; the oxygen to uranium ratio is also derived from the weight of U_3O_8 [37], in a way similar to those currently practiced methods of O/Me ratio determination for uranium, plutonium and mixed oxides [38, 39].

3.3.3. Water content

The moisture is determined by the well-known Karl Fischer titrimetric method where the end point is detected potentiometrically in a methanol medium [40].

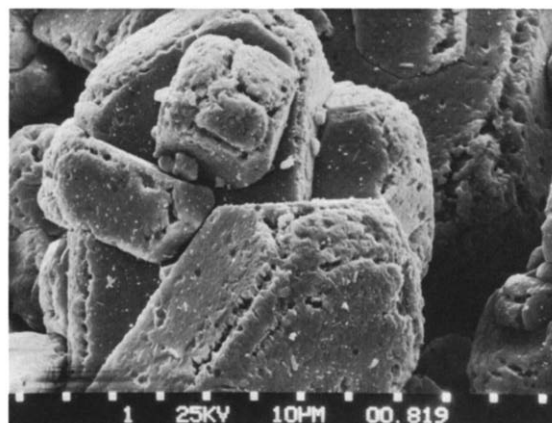


Fig. 1. Scanning electron micrograph of AUC powder produced from UF_6 in the pilot plant of IPEN.

4. Physical methods

4.1. Phase characterization

Since uranium oxides have a high tendency to become non-stoichiometric, the phase characterization of uranium oxides becomes a very important control of the process, especially during the establishment of a specific process route for oxide fuel production. In the step where the UO_2 is made chemically passive, for instance, X-ray diffractometry is very helpful for setting the process of oxidation to about $\text{UO}_{2.10}$. Therefore, the phase characterization by X-ray diffractometry becomes an important tool for control if it is realized promptly in an appropriate process step, even if only qualitatively.

IPEN has established a routine programme for obtaining X-ray diffraction pattern of powders sampled in different steps of UO_{2+x} preparation from ammonium diuranate (ADU) or ammonium uranyl carbonate (AUC). The uranium compounds U_3O_8 , UO_{2+x} , $\text{U}_3\text{O}_8 + \text{UO}_{2+x}$, ADU and AUC are quickly characterized qualitatively. Figs. 1 and 2 show the SEM-micrographs of AUC and UO_2 powders, respectively, produced in the pilot plant of IPEN.

Besides routine X-ray diffraction activities, a more elaborate diffraction profile analysis is being performed in the X-ray diffraction laboratory such as characterization of interdiffusion stages of (U, Th) O_2 solid solutions [41] and the mean crystallite dimension analysis of $\text{UO}_{2.10}$ powder for process control [42]. A version of an X-ray diffraction method for fuel characterization developed at Karlsruhe Nuclear Center for homogeneity determination of uranium-plutonium mixed oxides [43–46] was

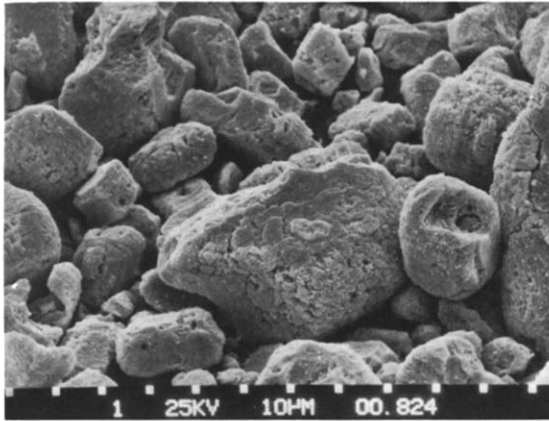


Fig. 2. Scanning electron micrograph of UO_2 powder produced by AUC decomposition in a static-bed furnace.

also implanted in our laboratory to be applied in uranium–thorium mixed oxides.

4.2. Surface area

The specific surface area is determined in uranium oxide powder by nitrogen adsorption in a commercial equipment. A mixture of helium and 10% nitrogen is passed over the sample that is weighed and cooled in liquid nitrogen. Nitrogen from the gas stream is adsorbed onto the sample, altering the composition of the gas mixture; this variation is detected by a thermal conductivity detector which is connected to a potentiometric recorder and measured by an electronic integrator.

A new commercial equipment, the AREA-meter based on the volumetric measurement of isothermally adsorbed nitrogen amount [28,47], according to Brunauer, Emmett and Teller (BET), serves for the routine determination of specific surface area in UO_2 powder.

4.3. Flowability and granulometry (sieve test)

A weighed UO_2 powder is filled in a funnel with defined side angle and orifice. The time necessary for the powder sample to pass through the funnel is measured. The pourability is specified as the time needed per 20 g UO_2 powder to flow through the lower orifice of the funnel.

The sieve test is performed with a hand-brush standard sieve.

4.4. Bulk density and tap density

A portion of UO_2 powder is allowed to fall through a funnel of standard dimension into a tared cup, up to the

mark, which defines a distinct volume. The bulk density is calculated from the weighed amount and the volume of UO_2 powder, according to ASTM B 212-82 [48].

After measuring the apparent density, the filled cup is mounted to a vibratory apparatus. The powder in the cylinder condenses according to a preset number of shocks. The tap density is calculated from the final volume and the known sample weight [28].

4.5. Density and microstructure

The density of the UO_2 pellet is determined by the immersion method. The bulk density and amount of open and closed porosity is performed by the penetration immersion method [28,47]. This method is based on the determination of the pellet volume and the volume of open and closed pores by measuring the dry mass, the saturated mass and the suspended mass of the sample.

The microstructure of the pellets is examined as follows. The pellet is longitudinally cut, polished and etched (chemically and thermally) following a way similar to standard procedure for quality control of UO_2 manufacture [28]. The microstructural examination is accomplished by light microscopy and scanning electron microscopy. A manual grain size analyzer is used for the determination of grain size and pore size distribution in a way somewhat archaic compared with recent development on image analysis for quantitative microstructural assessment [49–51], successfully applied to the nuclear fuel characterization [44,52].

4.6. Visual appearance and geometry

The visual appearance is examined either with the naked eye or under a low magnification viewer and compared to standards [28].

Surface roughness is measured with a commercial instrument which determines the center line average after an appropriate calibration with a standard [28]. For the pellet geometry examination, dial gauges, micrometers and air gauges are used. A commercial projection microscope is also used when an accurate characterization is required.

5. Conclusions

The characterization techniques that have been developed for the process and product control of fuel oxides in IPEN have yielded enough precision and accuracy required for the quality control and quality assurance stan-

dards necessary for the fabrication of UO₂ pellets to be employed in a PWR reactor.

The analytical techniques related to the measurements of the uranium isotopic ratio and the chemical properties have achieved necessary conditions to perform any specification control of uranium oxide pellets.

The laboratories of the physical properties determinations have been developed in a way conventional to perform specification control and process control of fuel oxides produced in the IPEN's pilot plant. In addition to the routine tasks, the X-ray diffraction laboratory realizes a more elaborate analysis of the crystallographic characteristics of fuel oxides. However for the laboratories of microstructural characterization, it is considered needful to have a facility to perform automatic image analyses for a better quantitative microstructural assessment.

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