Determination of U_3O_8 in UO_2 by infrared spectroscopy

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Abstract

The oxygen-uranium (O-U) system has various oxides, such as UO_2, U_4O_9, U_3O_8, and UO_3. Uranium dioxide is the most important one because it is used as nuclear fuel in nuclear power plants. UO_2 can have a wide stoichiometric variation due to excess or deficiency of oxygen in its crystal lattice, which can cause significant modifications of its proprieties. O/U relation determination by gravimetry cannot differentiate a stoichiometric deviation from contents of other uranium oxides in UO_2. The presence of other oxides in the manufacturing of UO_2 powder or sintered pellets is a critical factor. Fourier Transform Infrared Spectroscopy (FTIR) was used to identify U_3O_8 in samples of UO_2 powder. UO_2 can be identified by bands at 340 cm^{-1} and 470 cm^{-1}, and U_3O_8 and UO_3 by bands at 735 cm^{-1}, 910 cm^{-1}, respectively. The methodology for sample preparation for FTIR spectra acquisition is presented, as well as the calibration for quantitative measurement of U_3O_8 in UO_2. The content of U_3O_8 in partially calcined samples of UO_2 powder was measured by FTIR with good agreement with X-rays diffractometry (XRD).

Keywords: FTIR, uranium dioxide, triuranium octoxide.

1. Introduction

UO_2 is the most used nuclear fuel in nuclear power plants. It is manufactured in the form of sintered cylindrical pellets by powder metallurgy processes. It has been very well studied because it shows changes in its properties due to excess or deficiency of oxygen in wide stoichiometric ranges (O/U relation). O-U system presents various oxides, which have good dimensional stability under radiation and are chemically stable in a nuclear reactor environment.

The stoichiometry is very important for UO_2 performance as nuclear fuel. Fuel oxygen potential and O/U ratio have influence on mechanisms controlled by diffusion, such as grain growth, creep, release of fission gases, and thermal conductivity, in addition to chemical state and behavior of fission products. The O/U ratio increases with fuel burnup. Moreover, the sintering kinetics of UO_2 pellets is controlled by diffusion processes. Thus, the final characteristics of manufactured UO_2 pellets, which must be kept within very narrow limits, also depend on the O/U ratio of UO_2 powder. The O/U relation is an important parameter to be controlled, both in UO_2 powder and sintered pellets.

The chemical and physical properties of uranium oxides have been studied for many years using various techniques (Guéneau *et al.*, 2002). Small changes in stoichiometry produce considerable variation in uranium oxides, where uranium atoms can be in more than one oxidation state. During UO_2 manufacturing process, both as powder or pellets, all thermodynamically stable phases of O-U system may occur (UO_2, U_4O_9, UO_3, and U_3O_8). The presence of different phases also changes properties of UO_2 pellets and their thermodynamic performance as nuclear fuel.

Measurement of the O/U ratio is usually performed by gravimetric methods, which give partial information on UO_2 composition. It must be complemented by measures that identify the presence of other phases. X-rays diffraction is usually employed for phase identification and quantification. Nevertheless, it is hard to differentiate the uranium oxide patterns for angles between 20 and 40 degrees, especially at low levels. Thus, the use of X-ray diffraction to control the presence of other phases in UO_2 becomes impractical in an industrial process.

There are indications that infrared spectroscopy is very sensitive to the presence of phases in the O-U system, even at low levels. This technique is little explored for this purpose in the case of O-U system. The objective of this work was to exploit it in order to complement measurements of the O/U ratios. Since this technique is rapid and inexpensive, it has the potential to be used in the line production of UO_2 powder and pellets.

Allen *et al.*, (1976), noticed that infrared spectroscopy may be used to identify phases in O-U system based on bands observed between 1000 and 200 cm^{-1}. The conclusions of these authors were:

• The UO_2 infrared spectrum has a composite absorption of two components: a transverse optical phonon absorption, TO, at 340 cm^{-1} and a longitudinal optical absorption, LO, which causes a shoulder at 470 cm^{-1};

• When oxygen is incorporated into UO_2 crystalline lattice, the intensity TO/LO ratio increases;

• A solid solution of oxygen in UO_2 can be distinguished from a mixture of U_4O_9 and UO_2 by infrared spectroscopy;

• U_4O_9 has a weak band at 740 cm^{-1}. This band may be assigned to asymmetric stretching of continuous chains of uranium and oxygen atoms with the same -O-U-O-U- bond length. These strings do not exist in UO_2 fluorite lattice, such that no band is observed in this region. α-UO_3 and U_3O_8, which contain these chains, have intense bands at 740 cm^{-1}. U_4O_9 has a faint band, possibly due to early formation of these chains.

Axe and Pettit, (1966), measured infrared reflectivity of UO_2 single crystals. They notice a big difference in the region be-low 700 cm^{-1} compared to spectra obtained with UO_2 powder dispersed in the polymer matrix. This difference was attributed to the effect of dispersion of the infrared beam by particles of UO_2, which have diameters comparable to the wavelengths of incident infrared radiation.

In order to improve the visualization of UO_2 infrared spectrum, Allen *et al.*, (1976), acquired spectra at 5 K. No improvement was observed, thus showing that the bands are not due to thermodynamic effects. To visualize the band at 500 cm^{-1} of U_4O_9, Allen and Holmes, (1994), had dispersed 3 parts of oxide in 100 parts of KBr. In other oxides samples the dispersion was 1 part of oxide in 100 parts of KBr. The band at 450 cm^{-1} in U_4O_9 spectrum was attributed to the fact this oxide is the only one to show mixed valences. The bands at 425 cm^{-1} and 510 cm^{-1} were assigned to U_3O_7, respectively β-U_3O_7 and γ-U_3O_7. Ohwada and Soga, (1973), reported a strong band of α-U_3O_8 at 735 cm^{-1}. Hoekstra and Siegel, (1973), attributed this band to possible hydration of the oxide, which would have the kind of deformation U-O-H chain.

2. Materials and methods

UO_2 powder was provided by IPEN - Institute of Energy and Nuclear Research. U_3O_8 powder was obtained at CDTN by calcining UO_2 powder in air for 3 hours at 400°C. Fourier Transform infrared spectroscopy (FTIR) was performed with a BOMEM spectrometer, model MB102, in the 7000-400 cm^{-1} range with resolution of 8 cm^{-1} and 64 scans, at absorbance mode. Due to the intense absorption of infrared radiation by the uranium oxides, it was nec-essary to disperse the samples in KBr powder (Sigma Aldrich, spectroscopic grade, 99.99% purity). For a given KBr mass 1% mass of uranium oxide was diluted.

The mixtures of UO_2 and U_3O_8 powders shown in Table 1 were prepared to calibrate the FTIR spectra and to be used as reference for the quantitative analysis with XRD. Figure 1 shows the FTIR spectra of pure UO_2 and pure U_3O_8. The band at 735 cm^{-1} is related only to U_3O_8. The intensity of this band in the spectra of UO_2/U_3O_8 mixtures was used to estimate the content of U_3O_8. The regression of the calibration curve was performed with Minitab 17.

The XRD diffractograms were obtained with a RIGAKU X-ray diffractometer, model D/MAX-ULTIMA and the quantitative analysis of the UO_2 and U_3O_8 mixtures was carried out considering (001) peak by the RIR (reference intensity ratio) method using JADE 9.0 software.

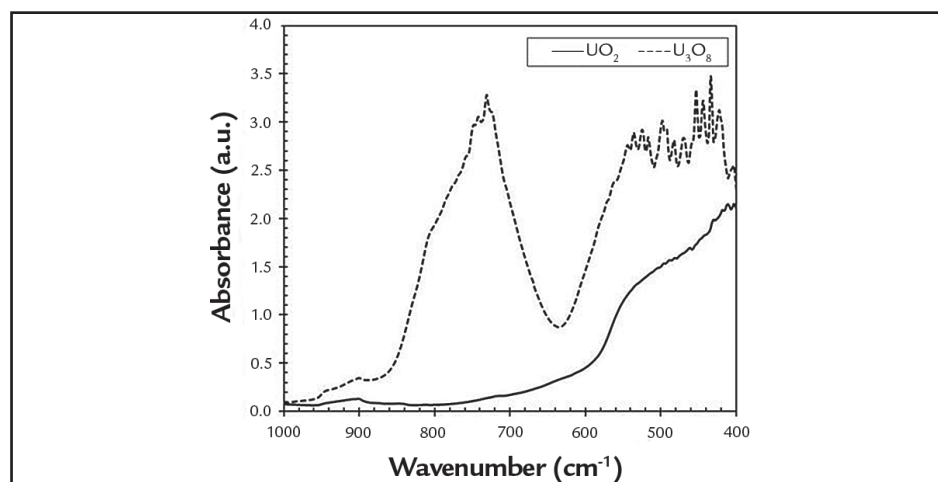| UO_2 (w/o)	99	97	95	93	90	80	60	40	20
U_3O_8 (w/o)	1	3	5	7	10	20	40	60	80

Table 1
Mixtures of UO_2 and U_3O_8
used to calibrate the FTIR spectra.

Figure 1
FTIR spectra of UO_2 and U_3O_8 powder.

To obtain an unknown mixture of UO_2 and U_3O_8 powders, 7.0 g of UO_2 powder samples were partially calcined in air at 300, 310, 320, 330 and 340 °C for two hours with a 10 °C/min heating rate in a muffle furnace. The calibrated FTIR and RIR method using JADE 9.0 software were used to estimate the U_3O_8 content in these calcined UO_2 samples.

3. Results and discussion

Table 2 shows values (absolute and relative to 100% U_3O_8) of intensity of the band at 735 cm^{-1} of known UO_2 and U_3O_8 mixtures as a function of U_3O_8 concentration.

Figure 2 shows the linear regression correlating U_3O_8 content with relative absorbance at 735 cm^{-1} (confidence level of 95%). The linear model can be expressed by:

$$rel.abs.735=(0.0494\pm0.0089)+(0.0089\pm0.0002)\times w/o.U_3O_8 \tag{1}$$

Table 2
Intensity of the band at 735 cm^{-1} of mixtures of UO_2 and U_3O_8 powders.

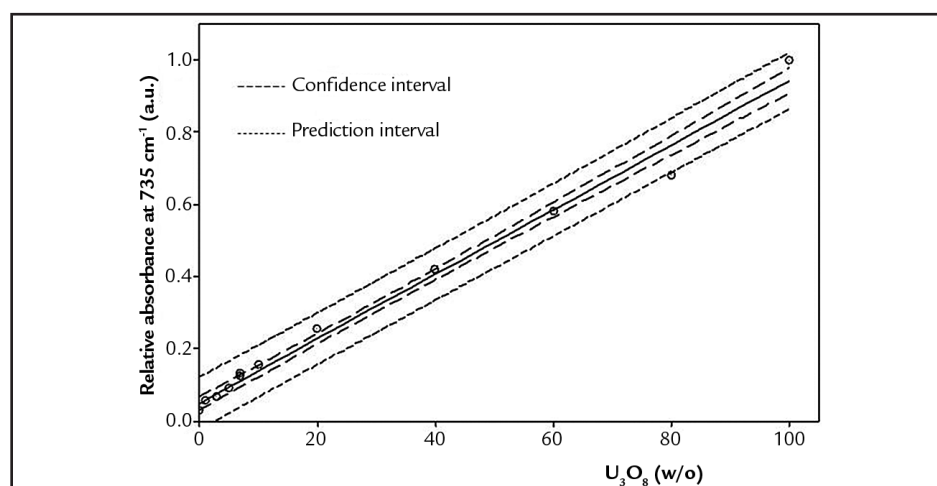| U_3O_8 w/o	Replica	735 cm^{-1} band intensity a.u.	735 cm^{-1} band intensity relative to 100 w/o U_3O_8	U_3O_8 w/o	Replica	735 cm^{-1} band intensity a.u.	735 cm^{-1} band intensity relative to 100 w/o U_3O_8
0	1	0.080	0.032	10	1	0.392	0.158
	2	0.078	0.031		2	0.393	0.159
	3	0.078	0.031	20	1	0.638	0.258
	4	0.077	0.031		2	0.633	0.256
1	1	0.141	0.057	40	1	1.038	0.420
	2	0.144	0.058		2	1.040	0.420
3	1	0.169	0.068	60	1	1.439	0.582
	2	0.171	0.069		2	1.440	0.582
5	1	0.230	0.093	80	1	1.685	0.681
	2	0.229	0.093		2	1.686	0.681
7	1	0.326	0.132	100	1	2.474	1.000
	2	0.311	0.126		2	2.475	1.000

Figure 2
Linear correlation model for the relative absorbance at 735 cm^{-1} and the content of U_3O_8 (α = 0.95).

U_3O_8 content in partially calcined UO_2 powder was estimated by FTIR using Equation 1. The results are shown in Table 3 compared with determinations obtained by X-rays diffractometry (DRX). Figure 3 shows that the agreement is quite good.

This method can also be extended to other oxides of the O-U systems, like UO_3 (band at 910 cm^{-1}) or U_4O_9.

Calcining temperature (°C)	Relative absorbance at 735 cm^{-1}	Estimated U$_3$O$_8$ content (w/o)	
		FTIR	DRX
300	0.365	35.46±2.07	43.6
310	0.543	55.46±2.52	57.2
320	0.697	72.76±2.91	80.3
330	0.826	87.26±3.24	93.1
340	0.923	98.16±3.48	99.3

Table 3
Estimation of U$_3$O$_8$ in partially calcined UO$_2$ powder (FTIR versus DRX).
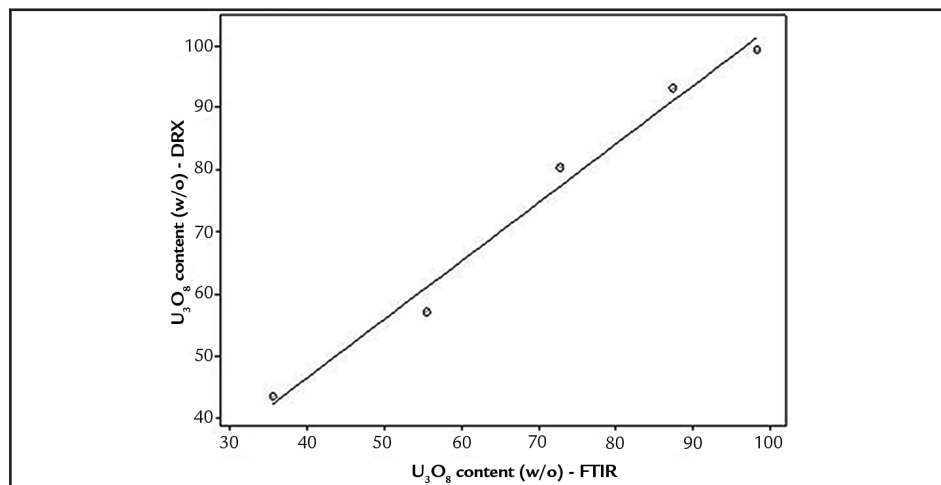

Figure 3
Comparison of measurement of U$_3$O$_8$ concentration in partially calcined UO$_2$ powder (DRX versus FTIR).

4. Conclusion

Fourier Transform Infrared Spectroscopy (FTIR) was used to measure contents of U$_3$O$_8$ in partially calcined UO$_2$ powders with good agreement with X-rays diffratometry measurements. A methodology for preparing uranium oxide samples for FTIR and XRD measurement was presented. Due to its low cost, simplicity, and rapidity, FTIR may be considered to complement O/U ratio measurements by gravimetric methods in UO$_2$ powder and pellet manufacturing. This technique may also be extended to other uranium oxides, like UO$_3$ or U$_4$O$_9$.

Acknowledgments

References

ALLEN, G. C., CROFTS, J. A., GRIFFITHS, A. J. Infrared spectroscopy of the uranium/oxygen system. *Journal of Nuclear Materials,* v. 62, n. 2-3, p. 273-281, 1976.

ALLEN, G. C., HOLMES, N. R. Characterization of binary uranium oxides by infrared spectroscopy. *Applied Spectroscopy,* v. 48, n. 4, p. 525-530, 1994.

AXE, J. D., PETTIT, G. D. Infrared dielectric dispersion and lattice dynamics of uranium dioxide and thorium dioxide. *Physical Review,* v. 151, n. 2, p. 676-680, 1966.

GUÉNEAU, C., BAICHI, M., LABROCHE, D., CHATILLON, C., SUNDMAN, B. Thermodynamics assessment of uranium-oxygen system. *Journal of Nuclear Materials,* v. 304, n. 2-3, p. 161-175, 2002.

HOEKSTRA, H. R., SIEGEL, S. The uranium trioxide-water system. *Journal of Inorganic and Nuclear Chemistry,* v. 35, n. 3, p. 761-779, 1973.

OHWADA, K., SOGA, T. Uranium-oxygen lattice vibrations of triuranium octoxide. Spectrochimica Acta Part A: *Molecular Spectroscopy*, v. 29, n. 5, p. 843-850, 1973.