

ANALYSIS OF HYDROGEN, CARBON, SULFUR AND VOLATILE COMPOUNDS IN (U_3Si_2 –Al) NUCLEAR FUEL

Sergio C. Moura, Marcelo M. Redígolo, Priscila O. Amaral, Claudio Leão, Glauca A. C. de Oliveira and Oscar V. Bustillos

Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP)
Centro de Química e Meio Ambiente (CQMA)
Av. Professor Lineu Prestes 2242
05508-000 São Paulo, SP
ovega@ipen.br

ABSTRACT

Uranium silicide U_3Si_2 is used as nuclear fuel in the research nuclear reactor IEA-R1 at IPEN/CNEN, São Paulo, Brazil. The U_3Si_2 is dispersed in aluminum reaching high densities of uranium in the nucleus of the fuel, up to 4.8 gU cm^{-3} . This nuclear fuel must comply with a quality control, which includes analysis of hydrogen, carbon and sulfur for the U_3Si_2 and volatile compound for the aluminum. Hydrogen, carbon and sulfur are analyzed by the method of Radio Frequency gas extraction combustion coupled with Infrared detector. Volatile compounds are analyzed by the method of heated gas extraction coupled with gravimetric measurement. These methods are recommended by the American Society for Testing Materials (ASTM) for nuclear materials. The average carbon and sulfur measurements are $30 \text{ } \mu\text{g g}^{-1}$ and $3 \text{ } \mu\text{g g}^{-1}$, respectively, and $40 \text{ } \mu\text{g g}^{-1}$ for volatile compounds. The hydrogen analyzer is a TCHEN 600 LECO, carbon and sulfur analyzer is a CS 244 LECO and the volatile compounds analyzer is a home-made apparatus that use a resistant furnace, a gas pipe measurement and a glove-box with controlled atmosphere where an analytical balance has been installed, this analyzer was made at IPEN laboratory.

1. INTRODUCTION

The research nuclear reactor IEA-R1 operating at “Instituto de Pesquisas Energética e Nucleares - IPEN/CNEN-SP” is a pool type reactor. It operates at 5 MW power and produces a large range of radioisotopes to supply the radiopharmaceutical need in the Brazilian nuclear medicine. The reactor fuel is composed of plates made of U_3O_8 – Al dispersion with 2.3 gU cm^{-3} and U_3Si_2 – Al that can reach 4.8 gU cm^{-3} [1]. The quality control of nuclear fuel is a major item to assure that all these components will work within the technical specifications in a nuclear plant [2, 3]. The gases occluded in the nuclear fuel, under the operation conditions of the reactor, are released and affect the performance of the fuel and clad. The Hydrogen, Carbon, Sulfur and volatile compounds are items that are monitored in this quality control.

2. METHODOLOGY

The hydrogen, carbon and sulfur are analyzed by the method of Radio Frequency (RF) gas extraction combustion coupled with Infrared (IR) and thermal conductivity (TC) detectors. The volatile compounds are analyzed by the method of heat gas extraction coupled with

gravimetric measurement [4]. These methods are recommended by the American Society for Testing Materials (ASTM) for nuclear materials [5]. Besides these gases, Oxygen and Nitrogen are also detected and quantified by these analyzers.

The hydrogen, oxygen and nitrogen are detected by the analyzer model TCHEN 600 from LECO Co. and the carbon and sulfur are detected by the analyzer CS400 from LECO Co. These analyzers employ different techniques to detect these gases.

2.1 Hydrogen, oxygen and nitrogen analyses

The TCHEN 600 determines the hydrogen, nitrogen and oxygen content of a sample. It uses a self-contained electrode furnace for fusion. Hydrogen and Oxygen are measured by infrared detection as carbon dioxide, carbon monoxide and water vapor in an IR cell. Nitrogen is measured by thermal conductivity in a TC cell. Analysis begins by placing an empty graphite crucible on the lower electrode. The electrodes dose and atmosphere is purged from the crucible. High current passes through the crucible generating heat, which drives off gasses trapped in the graphite. This process is called outgassing. Then, a sample is dropped from the loading mechanism into the crucible. High current is again passed through the crucible driving off gasses in the sample. To prevent further outgassing during analysis, a current lower than outgas current is used [6].

Oxygen is measured by IR absorption. Sample gases first enter the IR module and pass through CO and CO₂ detectors. Oxygen is detected as either CO or CO₂. Following this, the gas sample is passed through heated copper oxide to convert CO to CO₂ and any hydrogen to water. Gases then re-enter the IR module and pass through a separate CO₂ detector for total oxygen measurement. This configuration maximizes performance and accuracy for both low and high range. The instrument automatically chooses the optimum detection range.

Nitrogen is measured by thermal conductivity. Sample gases pass through heated copper oxide which converts CO to CO₂ and hydrogen to water. CO₂ and water are then removed with a Lecosorb/Anhydrone trap to prevent detection by the TC cell. Gas flow then passes through the TC cell for nitrogen detection.

Hydrogen is measured by infrared absorption. Sample gases pass through heated copper oxide which converts CO to CO₂ and hydrogen to H₂O. Gases enter the IR module and pass through an H₂O detector for total hydrogen measurement. As CO₂ is trapped by Lecosorb, the sample gas flow rate is reduced. The dynamic flow compensator adds carrier gas to the sample gasses, maintaining a constant flow rate. In the presents of high oxygen, this process improves the nitrogen sample results.

After the dynamic flow compensator, sample gasses flow through the measure flow scrubber where carbon dioxide is removed by Lecosorb to prevent detection by the Te cell. Water vapor is formed when carbon dioxide is trapped. Since water vapor can be detected by the TC cell, Anhydrone is used to remove it. Sample gasses then flow through TC cell producing the nitrogen result [13].

2.2 Infrared absorption and detection

The infrared source consists of nickel-chrome wire that is resistance heated to 850°C. The IR source radiates visible energy as well as all of the wavelengths in the infrared spectrum. Oxygen is detected in the IR cells as carbon monoxide or carbon dioxide. Carbon oxides absorb IR energy at a precise wavelength within the IR spectrum [7]. Energy from the IR source is absorbed as the gas passes through the cell, preventing it from reaching the IR detector. All other IR energy is prevented from reaching the IR detector by a narrow band pass filter. Because of the wavelength filter, the absorption of IR energy can be attributed only to one carbon oxide. The concentration of carbon dioxide is detected as a level of energy at the detector.

One IR cell is used as both a reference and measurement. The total oxygen, as carbon dioxide and carbon monoxide, is detected on a continuous and simultaneous basis. The cell consists of an IR source, a narrow band-pass filter, a condensing cone, an IR energy detector, and the cell body. Radiated energy enters the cell body through a window, travels through the cell body, and then exits through a second window and a precise wavelength filter. The selective filter passes only the carbon dioxide absorption wavelength into a condensing cone, which concentrates the energy at the detector. As the gas concentration increases the voltage to the preamplifier decreases. The starting reference level, or "baseline," for the detector is established by running helium through the cell. The pure helium environment permits the maximum amount of energy to reach the detector. This maximum energy level is coupled to the preamplifier where it is amplified and filtered. It is then sent to an analog to digital (AD) converter where it is converted to a digital signal.

2.3 Thermal conductivity detection

The Thermal Conductivity Cell can determine the differences in the thermal conductivity of gases. The cell consists of two matched filaments that are maintained in a constant gas flow. Only the gas type is different. The reference filament is subjected to only carrier gas, while the measurement filament is subjected to the sample gas mixed with carrier gas. The cell output is zero while both filaments are in identical carrier gas environments. The filament current causes the filaments to self-heat and keeps the filament temperature higher than the ambient oven temperature. The oven temperature is maintained at 50°C, which eliminates the effects from normal room temperature variations. As long as both resistors remain in the same environment, the cell output will remain at zero. Any disturbance of this environment will result in a change or increase in output. The output is zero when helium flows in both chambers of the cell. The introduction of nitrogen will cause the temperature of the measure filaments to increase because nitrogen has a lower thermal conductivity than helium. This causes the current through the filament to change, producing an output. The magnitude of the output will vary due to the concentration of nitrogen. Like the IR cell, the output from the TC cell is fed to a preamplifier. This, in turn, is fed to an analog to digital converter. The output, a digital signal, is then fed to the computer where it is processed, displayed, and stored as the nitrogen measurement result [8].

2.4 Carbon and Sulfur analyzer

The CS-400 Carbon and Sulfur Analyzer is a microprocessor based, software driven instrument for measurement of Carbon and Sulfur content in metals, ores, ceramics and other inorganic materials. The CS-400 uses the HF-400A induction furnace and measures carbon and sulfur by infrared absorption. Analysis begins by weighing out a sample into a ceramic crucible on the built-in balance. A tungsten alloy is added as accelerator material, the crucible is placed on the loading pedestal. Furnace closure is performed automatically, then, the combustion chamber is purged with oxygen to drive off residual atmospheric gases. After purging, oxygen flow through the system is restored and the induction furnace is turned on. The inductive elements of the sample and accelerator couple with the high frequency field of the furnace. The pure oxygen environment and the heat generated by this coupling cause the sample to combust. During combustion all elements of the sample oxidize. Carbon bearing elements are reduced, releasing the carbon, which immediately binds with the oxygen to form CO or CO₂. Also sulfur bearing elements are reduced, releasing sulfur, which binds with oxygen to form SO₂.

Sample gases are swept into the carrier stream. Sulfur is measured as sulfur dioxide. Carbon monoxide is converted to carbon dioxide in the catalytic heater assembly while sulfur trioxide is removed then the system in a cellulose tilter trap Carbon is measured as carbon dioxide in the IR cells, as gases flow through the IR cells [9].

3. EXPERIMENTAL

The nuclear fuel U₃Si₂-Al sample is split into two masses, one goes to the analyzer TCHEN 600 for the detection of hydrogen, oxygen and nitrogen and the other goes to the CS-400 analyzer for the carbon and sulfur [10].

Figure 1 shows the spectra of the hydrogen, nitrogen and oxygen detected by the TC and IR detectors. These spectra are used to quantify the hydrogen, oxygen and nitrogen in the nuclear fuel.

The carbon and sulfur are analyzed by the CS-400 using the Infrared absorption detector.

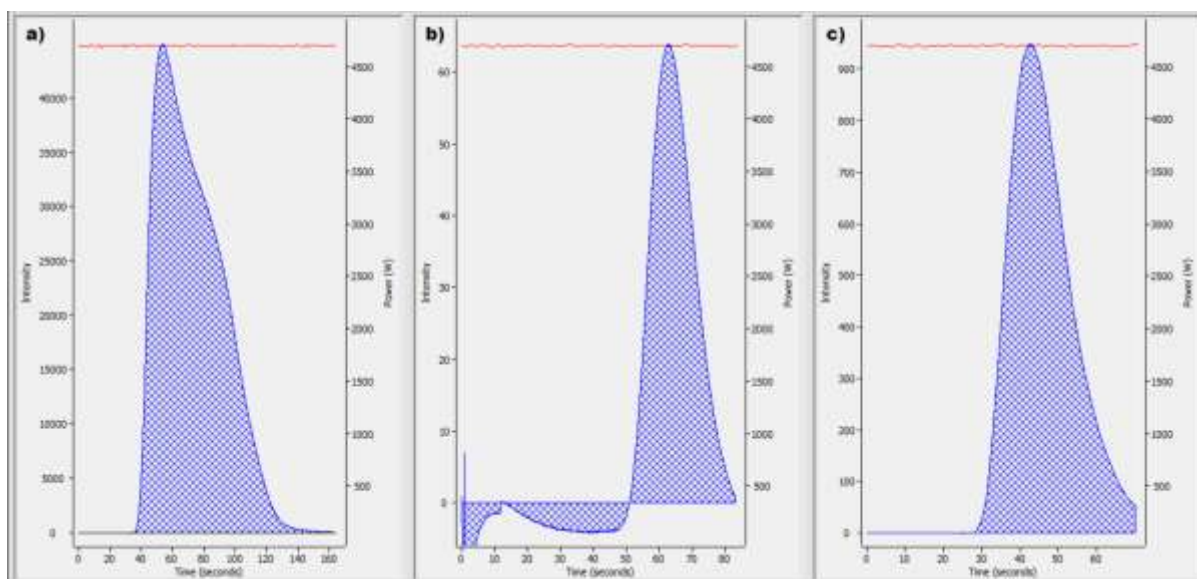


Figure 1: Spectra of the TECHEM: Hydrogen (a), Nitrogen (b) and Oxygen (c).

3.1 Statistical laboratory program

A statistical laboratory program has been set to validate the data generated in the nuclear fuel material to specify any agreement with the recommended ASTM methods. The validation program is applied in the IPEN laboratories for assessing how the results of a statistical analysis will generalize to a reliable data set. The validation program set many statistical parameters such as selectivity, linearity, detection limit, quantification limit, precision and accuracy. These parameters are defined by two agencies in Brazil, namely, ANVISA (Agência Nacional de Vigilância Sanitária) and INMETRO (Instituto Nacional de Metrologia, Normalização e Qualidade Industrial) [11,12].

4. RESULTS AND DISCUSSION

Table 1 presents the results of two nuclear $U_3Si_2 - Al$ fuel elements, where the Carbon, Sulfur and volatile compounds were analyzed. Carbon and Sulfur were determined using method of Radio Frequency gas extraction combustion coupled with Infrared detector. Volatile compounds were determined using method of heat gas extraction coupled with gravimetric measurement. The results show that the fuel elements are below the maximum limit established by the nuclear quality control manual.

The statistical results show precision and accuracy in the range of 10%. These results comply with the ASTM mandatory regulation for the nuclear fuel in the manual of the quality assure for $U_3Si_2 - Al$ nuclear fuel.

The average Carbon is $30 \mu g g^{-1}$ and Sulfur is $3 \mu g g^{-1}$. The average for volatile compounds is $40 \mu g g^{-1}$.

Table 1: Carbon, Sulfur and volatile compounds in U₃Si₂ – Al nuclear fuel

Fuel element ($\mu\text{g g}^{-1}$)	1	2
Carbon	33 \pm 2	35 \pm 3
Sulfur	2.0 \pm 0.1	6.0 \pm 0.2
Volatile compounds	40 \pm 5	36 \pm 2
Hydrogen	26.7 \pm 2.9	35.2 \pm 2.7
Nitrogen	46 \pm 3	14 \pm 3
Oxygen	1115 \pm 70	2052 \pm 10

5. CONCLUSIONS

These results represent a satisfactory performance of the fuel inside the nuclear reactor. The quality control of the nuclear fuel with reference to gases is completed with the analysis of Hydrogen, Nitrogen and Oxygen, which have been reported elsewhere [8]. All the nuclear fuel is mandatory to quality control testing of gases to assure a good performance of the fuel inside the nuclear reactor IEA-R1 located in “Instituto de Pesquisas Energéticas e Nucleares” (IPEN), São Paulo, Brazil.

REFERENCES

1. M. Durazzo, J. A. B. Souza, “Fabrication technology on high uranium loaded dispersion fuel elements”, *Proceedings of INAC-2011*, Belo Horizonte, October 24, **Vol.1** (2011).
2. J. Khan, D. D. Kaiser, B. D. Miller, J. F. Jue, A. B. Robinson, J. W. Madden, P. G. Medved, D. M. Waches, “Microstructure of the irradiated U₃Si₂-Al silicide dispersion fuel”, *J. Nucl. Mat.*, **Vol. 419**, pp.97-104 (2011).
3. R. C. Birtcher, J. W. Richardson, R. H. Mueller, “Amorphization of U₃Si₂-Al by ion or neutral irradiation”, *J. Nucl. Mat.*, **Vol. 230**, pp.158-163 (1996).
4. Y.S. Sayi, V.C.S. Yada, P.S.S. Shankaran, “Total gas analysis of nuclear fuel”, *Indian Journal of Chemistry Technology*, **Vol. 11**, Issue 5, pp.648-653 (2004).
5. AMERICAN SOCIETY OF TESTING MATERIAL - ASTM, Standard test method for the determination of total hydrogen content of uranium oxide powders and pellets by carrier gas extraction. C1457. (2011).
6. T. Crewe, P.C. Lopes, S.C. Moura, J.A.G. Sampaio and O.V. Bustillos, “Characterization of Hydrogen, Nitrogen, Oxygen, Carbon and Sulfur in Nuclear Fuel (UO₂) and Cladding Nuclear Rod Materials”, *Proceedings of INAC-2011*, Belo Horizonte, October 24, **Vol.1** (2011).
7. D.L. Pavia, G.M. Lampman, G.S. Kriz and J.R. Vyvyan, “Introduction to spectroscopy”. Ed. Cengage Learning. New York. (2010).
8. O. Vega, H.G. Riella, C. Rodrigues “Quantitative analysis of occluded gases in UO₂ pellets by quadrupole mass spectrometer and its application in quality control of nuclear fuel”, *Journal of Nuclear Material*, **Vol. 106**, pp.121-125 (1982).
9. O. Vega Bustillos “Utilização da técnica de espectrometria de massa na análise de gases oclusos em pastilhas de dióxido de urânio” Dissertação de Mestrado. IPEN/CNEN. (1980).
10. O. Vega, K. Imakuma “Determinação do oxigênio, nitrogênio e hidrogênio oclusos no Zircaloy-4 pela técnica da extração a vácuo acoplada a cromatografia a gás” *Revista Brasileira de Aplicação de vácuo*, **Vol. 3**, Num. 1 - 2, pp.153-160 (1983).

11. ANVISA, Agência Nacional de Vigilância Sanitária, “Guia para validação de métodos analíticos e bioanalíticos”, Resolução RE n. 899, (2003).
12. INMETRO, Instituto de Metrologia, Normalização e Qualidade Industrial. “Orientação sobre Validação de Métodos de Ensaio Químicos” DOQ-CGCRE-008. Revisão 04 (2011).M.T.I.
13. A. Maeda, T. Iwai, T. Omichi. “Residual gas analyses in oxide nuclear fuel” IAEATecdoc. **Vol. 466**, pp. 34 (1987).
14. Y.S. Sayi, P.S. Ramanjaneyulu, C.S. Yadav, P.S. Shankaran, G.C. Chapru, K.L. Ramakumar, V. Venugopal “Release of gases from uranium metal at high temperatures” *Journal of Nuclear Materials*, **Vol. 373**, pp.75–81 (2008).
15. S. C. Moura, C. E. Fernandes, J. P. R. Oliveira, L. M. Guglielmo, O. V. Bustillos. “Total and occluded residual gas content inside the nuclear fuel pellets”. In: INAC (International Nuclear Atlantic Conference), Rio de Janeiro. Innovations in Nuclear Technology for a Sustainable Future, (2009).