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# Raman Spectroscopy, a Useful Tool to Study Nuclear Materials

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#### Abstract

The use of the Raman technique is nowadays being widely spread in many scientific and industrial disciplines. The rise of this spectroscopy is due to the technology developed in some of its main components (the laser, charge-coupled device (CCD) sensors, gratings, filters, etc.), what reduces the cost of the equipment. Characterization by Raman spectroscopy has long and well-established tradition in fields such as condensed matter physics and chemistry. In nuclear sciences, by contrast, it is far from being extensively applied, even though this technique can be especially useful. It is a fact that only a scarce number of Raman laboratories dealing with nuclear materials exist, and therefore a limited database related to these materials. In such a context, this chapter is devoted to the practical use of Raman spectroscopy for nuclear materials characterization.

Keywords: Raman, nuclear, uranium oxides, U-secondary phase

# 1. Introduction

Nuclear power is a controversial subject that generates a debate in today's society; nevertheless, the existing 438 nuclear reactors [1] produce approximately 15% of the world's electricity [2], making it a major world energy source.

Proponents of nuclear energy describe nuclear power production as a low running costs and a nature friend since it can be considered a low carbon technology compared with fossil fuels such as coal, gas, and oil [3]. Opponents of nuclear power argue that this energy has very high initial costs, complex nuclear waste management, and high plant decommissioning costs, and



© 2016 The Author(s). Licensee InTech. This chapter is distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/3.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. (co) BY highlight the environmental and public risks and dangers associated with it [4, 5]. This debate has been mirrored by the number of nuclear power plant (NPP) constructions. For example [6], before the accident in Fukushima Daiichi in 2011, the number of NPPs was increasing due to the concerns over greenhouse gas emissions to avoid further global warming. Then, the accident impacted public acceptance of nuclear power and had an effect of decreasing the number of nuclear reactors [7]. In recent years, the number of constructions commencing are on the rise again [8], and the main concern is related to the nuclear waste management, mainly spent nuclear fuel (SNF).

The most common nuclear fuel consists of uranium dioxide,  $UO_2$ , enriched from 0.7 to 3–5% of <sup>235</sup>U depending on which reactor it will be loaded into [9]. After its irradiation in the reactor core, the fuel is composed of a matrix of  $UO_2$  (>95%) doped with fission products and transuranium elements [10], which are found as bubbles (Xe, Kr), metallic precipitates (Mo, Tc, Ru, Rh, and Pd), oxide precipitates (Rb, Cs, Ba, and Zr), solid solutions, and transuranium elements dissolved by U substitution in the  $UO_2$  matrix [11]. These elements are not distributed homogeneously as a consequence of the thermal gradient within the  $UO_2$  pellet (temperature as high as 1700°C at the center of the pellet and decreasing to 400°C outwards) [12, 13]. Besides, the spent nuclear fuel suffers substantial microstructural modifications from the initial fresh fuel such as coarsening of the grains and extensive microcracking. Thus, SNF can be described as a complex, hot, and radioactive waste and therefore extremely dangerous. Bruno et al. [14] provide a particularly suitable example to demonstrate how hazardous the SNF is, that is, ...."One year after discharge from a reactor...a person exposed to this level of radioactivity at a distance of one meter would receive a lethal dose in less than one minute...."

After several thousands of years, the total radioactivity of the SNF equals the radioactivity of natural uranium [15]. Therefore, within the management of spent nuclear fuel, the safe storage of this radioactive waste from the discharge of the reactor until the decay reaches natural uranium radioactivity is considered. Countries adopt different stages of these nuclear storages according to their internal policies [16], but usually the following steps are suitable: (i) spent fuel pools [17], (ii) intermediate storage or reprocessing [18], and (iii) final storage [19].

After SNF is removed from the reactor, it is stored for the first few years on-side in water containers or pools, located close to the reactor in order to allow the spent fuel to decay, both radioactively and thermally. Then, it can be transported to a reprocessing facility or to a definitive storage facility. However, since final repositories for spent fuel do not exist for the moment, interim storage is required. NPPs use the spent fuel dry-cask storages, which are steel and concrete containers filled with an inert gas as a first step for interim storage. Although no ultimate storage in operation exists, the deep geological repository is internationally accepted as the best solution [20].

The performance of the mentioned repositories requires knowledge of the SNF stability at different storage conditions. Thereby, the studies of the spent fuel behavior can be mainly divided into dry and wet conditions, given the different evolution observed in each case. The studies of spent nuclear fuel under dry conditions are mainly focused on the oxidation of both the  $UO_2$  matrix and the  $AnO_2$  [21] present in the SNF.<sup>1</sup> In case of shielding failure, the oxidation of  $AnO_2$  and  $UO_2$  takes place owing to its contact with the atmospheric oxygen and the high

temperatures present (up to 400°C) [15]. This oxidation occurs via oxygen incorporation into the fluorite structure (fcc) of the stoichiometric oxide, for example, some actinides as plutonium and uranium can oxidize to  $AnO_{2+x}$  (x < 0.25) maintaining the fcc structure [22]. Further oxidation to higher-oxidation states (V and VI) leads to different structures. For example, the transformation of  $UO_2$  into  $U_3O_8$  via the two-step reaction [23]  $UO_2 \rightarrow U_4O_9/U_3O_7 \rightarrow U_3O_8$  entails an increase in the volume of around 36% and, consequently, it might cause the loss of the  $UO_2$  matrix integrity.

On the other hand, the studies of spent nuclear fuel under wet conditions are focused on the corrosion process of this waste. This might happen in case the SNF shielding fails while stored in pools or in the deep geological repository at timescales of the order of some thousands of years [24] when it is assumed that the barriers that protect the waste will be breached and SNF will be in contact with water [25]. The  $UO_2$  matrix of the spent nuclear fuel might dissolve with water and then the release to the biosphere of the SNF radioactive contents might occur [26–28].

This corrosion process is primarily described by the oxidation of uranium,  $U(IV) \rightarrow U(VI)$ , and then the alteration products formation, usually containing  $UO_2^{2+}$  in their crystal structures [29]  $U(VI) \rightarrow UO_2^{2+}$  (s).

Great effort has been performed to analyze the reaction mechanism and to establish the key parameter that controls the corrosion of the SNF such as leaching/dissolution experiments [30–32] and studies of the uraninite, a natural analog of the spent nuclear fuel matrix [33, 34]. These stability studies require the characterization of the SNF and its reaction products, with  $O_2$  and/or water, which is a great challenge not only because these materials are very complicated (containing almost the entire periodic table) [11] but also because intense radiation field inherently associated to these materials makes it difficult to examine them in safe conditions.

In order to minimize radiation doses and the release of radioactive material, the working procedure employed to study these materials must fulfill the ALARA principle (acronym for "as low as reasonably achievable") [35]. Such a reliable procedure must, hence, minimize the time that radioactive materials are handled and maximize the distance to them. Raman spectroscopy is an analyzing technique that has been established in recent years as a useful tool since it fulfills the mentioned safe principles, as shown by the increase in the number of publications dealing with the characterization of nuclear materials by this technique [36–44]. This is due to some of its features as (1) that it does not require any special preparation of the sample, (2) it allows the analysis of a very small amount of sample, and (3) it is a nondestructive technique.

Besides these safety principles, the confinement of the whole apparatus in a glove box or a hot cell is also very common, which obviously complicates the measurements [45]. Despite the advantages mentioned above, the characterization of these SNF and related nuclear materials is far from being well established. Existing databases must be improved and new methods

<sup>1</sup> A meaning minor actinides such as Np, Pu, and Am.

must be developed. Due to the hazardous feature of nuclear materials, both the development of new protocols and Raman spectra acquisition (for the purpose of extending the databases) are usually performed first by analyzing the behavior of different SNF analogs and, once the method is feasible, by applying it to the real SNF. Such analogs can be divided into two kinds: synthetic analogs such as uranium dioxide (UO<sub>2</sub>) [46, 47] or SIMFUEL (simulated fuel) [48, 49], and natural analogs such as uraninite.

In this context, this chapter is structured as follows: In the first part, Raman spectroscopy is described. First, the theoretical aspects on an introductory level are explained. Second, the main components of the Raman spectrometers are presented and, as an example, the *LabRam HR Evolution* spectrometer is described in more detail. The "Results" section has been divided into two, corresponding to dry and wet conditions; in each part, the developed method and the results found for analogs of the SNF are shown. Namely, the materials studied in this section are the different uranium oxides,  $UO_{2+x}$  (0 < x < 0.25),  $U_4O_9/U_3O_7$ , and  $U_3O_8$ , and several secondary phases such as rutherfordine, soddyite, uranophane alpha, or kasolite.

## 2. Raman spectroscopy technique

### 2.1. Description of the Raman phenomena

Raman effect owes its name to the Indian physicist Chandrasekhara Venkata Raman [50] who won the Nobel Prize for its discovery. In his Nobel lecture, given on December 11, 1930, Sir C.V. Raman said..."The frequency differences determined from the spectra, the width and character of the lines appearing in them, and the intensity and state of polarization of the scattered radiations enable us to obtain an insight into the ultimate structure of the scattering substance [...]. It follows that the new field of spectroscopy has practically unrestricted scope in the study of problems related to the structure of matter" [51].

As other molecular spectroscopy techniques, Raman scattering is based on the analysis of lightmatter interaction [52], that is, absorption, emission, or scattering of a photon. Two interpretations of this phenomenon can be considered: the quantum mechanical method and the classical interpretation. In the purely classical interpretation, the radiation is considered as an electromagnetic wave, and the matter as an assembly of independent classical rotors and vibrators. This model can explain satisfactorily the main features of the light scattering such as the frequency dependence and some key aspect related to their selection rules.

Raman effect is described as an inelastical scattering of light. From a macroscopic point of view, light scattering consists in a deviation of light from its straight trajectory (original direction of incident light). Molecules scatter light because the electric field of the incident light wave forces the electrons within the molecule to oscillate (see **Figure 1**), producing oscillating electric moments leading to the reemission of radiation in all directions [53].



Figure 1. Light scattering produced by the interaction of the incident light's electric field and the molecule electrons.

Such process produces two types of radiation, Rayleigh radiation, which has the same frequency that the incident light ( $v_0$ ), and Raman radiation, which consists in a new set of frequencies with more or less energy than the incident radiation ( $v_0 \pm v_1$ ), where  $v_1$  is typically related to the rotational, vibrational, and electronic levels of the molecule. In **Figure 2**, a general scheme of the scattering process and its difference with the absorption process from the point of view of the photons and the energy levels of the molecule are represented.



**Figure 2.** Energy level diagrams describing the physical phenomenon of (1) IR absorption, (2) Rayleigh scattering, and (3) Raman scattering.

Before the interaction of the radiation with the system, there are N photons of energy  $hcv_0$ . In the case of the absorption process, the interaction of the radiation with the system leads to the excitation of the molecule to a higher energy state resulting in a radiation which consists in N – 1 photons of energy  $hcv_0$ . This process can occur, if and only if the incoming photon has the same energy as the difference between the initial and final state of the molecule,  $E_f - E_i = hcv_{fi} = hcv_0$ , fulfilling the condition of energy conservation.

Let us now consider the scattering process, the interaction between the incident radiation and the system produces the annihilation of a photon of energy  $hcv_0$ , and simultaneously the creation of a new photon with energy  $E_s$ . Now the radiation consists in N – 1 photons of energy  $hcv_0$ , a new photon of energy  $hcv_s$ , and the transition to the molecule to a final state with energy  $E_f$ . In the overall process, the energy must be conserved so,  $hcv_0 = hcv_s + E_f$ .

This two-photon process can be visualized as two simultaneous stages. First, the annihilation stage which leads the molecule to a virtual high-energy state. Virtual states are created when

the laser interacts with the molecule and causes polarization; hence, their energy is determined by the frequency of the incident light source used ( $v_0$ ). At this stage, there is no energy conservation implying that the role of the incident radiation in the scattering is to perturb the molecule given the possibility to allow different spectroscopic transitions rather than the absorption process. Second, the creation stage, where the molecule reaches its final state with energy  $E_{\rm f}$  producing the new photon. At this point, we can consider two types of scattered light: (1) the Rayleigh scattering, or elastic scattering, where the final state of the molecule is its own initial state,  $E_f = E_i$ , and, correspondingly, the energy of the scattered light corresponds to the initial frequency value,  $v_s = v_0$ . (2) The Raman scattering, or inelastic scattering, in which the molecule reaches a final state different from its initial state; hence, the energy of the scattered light has a different frequency value from the incident radiation,  $v_s = v_0 \pm v_{fi}$ . This process is much less probable than Rayleigh scattering (only 10<sup>-5</sup> – 10<sup>-8</sup> of the incident beam intensity). If the final state has a higher energy than the initial state,  $E_f > E_i$ , the scattered photon loses energy,  $v_s = v_0 - v_{fi}$ . This radiation is known as Stokes Raman scattering. By contrast, if the final state has a lower energy than the initial state,  $E_f < E_i$ , the scattered photon increases its energy,  $v_s = v_0 + v_{fr}$  giving the anti-Stokes Raman scattering. Relative probabilities of Stokes and anti-Stokes radiation depend on the population of the molecule states, f and i, and therefore on temperature according to the Maxwell-Boltzmann distribution. As both give the same information, it is customary to measure only the "Stokes" side of the spectrum.

Even though this general scheme describes scattering phenomena in a qualitative way, it highlights some key aspect of the Raman spectroscopy and its differences with the absorption process. Nevertheless, it is worth to describe the classical treatment of the Raman scattering in order to provide a deeper insight in the frequency dependence and the microscopic origin of the scattered light. Classical wave interpretation [54, 55] of the Raman effect is based on the time-dependent polarizability of the molecules. Consider one of the simplest scattering systems, a vibrating diatomic AB molecule.

Such a system can be modeled, at first approximation, as two balls attached by a spring (**Figure 3**). According to Hook's law, its relative movement can be described by the second Newton law as follows:



Figure 3. Simplified model of a diatomic AB molecule.

$$\mu \left(\frac{d^2 x_1}{dt^2} + \frac{d^2 x_2}{dt^2}\right) = K(x_1 + x_2)$$
(1)

where  $\mu$  represents the reduced mass of the molecule, *x* represents the displacement, and *K* represents the bond strength. For small vibrations, the harmonic approximation holds, and then the normal coordinates *q*(*t*) of the vibrating molecule can be expressed as

$$q = q_0 \cos(2\pi v_m t)$$
(2)  
where  $q_0$  is the amplitude and  $v_m$  is the natural vibration frequency which is defined in terms  
of its bond strength as  
$$v_m = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}}$$
(3)

When incident light interacts with a molecule, induces a dipole moment, *P*, equal to the product of the polarizability of the molecule,  $\alpha$ , and the electric field of the incident light source *E* 

$$P = \alpha E_0 \cos(2\pi v_0 t), \tag{4}$$

where  $E_0$  and  $v_0$  are the electric field amplitude and frequency, respectively. As far as the molecule is vibrating, its polarizability varies according to the relative displacement of these atoms and therefore we can express  $\alpha$  as a power series q

$$\alpha = \alpha_0 + q \left(\frac{\partial \alpha}{\partial q}\right)_0 + \dots$$
 (5)

which when combined with Eqs. (3) and (5) results in,

$$P = \alpha_0 E_0 \cos(2\pi v_0 t) + q_0 \cos(2\pi v_m t) E_0 \cos(2\pi v_0 t) \left(\frac{\partial \alpha}{\partial q}\right)_0$$
(6)  
$$P = \alpha_0 E_0 \cos(2\pi v_0 t) + \left(\frac{\partial \alpha}{\partial q}\right)_0 q_0 E_0 \left[\cos\left(2\pi \{v_0 - v_m\}t\right) + \cos\left(2\pi \{v_0 + v_m\}t\right)\right]$$
(7)

From Eq. (7), it is evident that the induced electric dipole is formed by three different terms. The first one gives rise to an oscillating moment at the same frequency of the incident light, the Rayleigh scattering, and two additional terms which accounts for the Stokes and anti-stokes Raman scattering. Therefore, Rayleigh scattering arises from an electric dipole which oscillates at the same frequency induced in the molecule by the electric field of the incident radiation,

whereas Raman scattering arises from the modulation of the electric dipole with the natural frequency of the vibrating molecule. This modulation is produced by the electrons of the molecule, whose rearrangement produces a coupling between the nuclear motion and the electric field of the radiation.

#### 2.2. Dispersive Raman spectrometer

From the basis of the Raman effect described above, it is easy to deduce that in a conventional (or dispersive) Raman spectrometer,<sup>2</sup> the main difficulty lies in separating the intense stray light of the Rayleigh scattering from the much weaker Raman-scattered light. Besides, as Raman scattering has low efficiency, the optimization of each of the instrumental components becomes critically important.

The main components of a Raman setup are as follows:

- (1) Excitation source
- (2) Sample illumination systems and collection optics
- (3) Wavelength selectors and separators
- (4) Detector
- (5) Recording device

1. *Excitation source:* Traditionally, mercury arc lamps were used as light sources until being replaced by laser sources. Laser beams are highly monochromatic, present small diameter and, with the help of different optic devices, can be focused on small samples. Different lasers can be used as the light source in Raman spectrometry, as the ones shown in **Table 1** [56].

Laser	Wavelength (nm)	
Ar ion	530.9/647.1	
He-Ne	632.8	
Near IR diode	785/830	
Nd-YAG	1064	
Frequency-doubled Nd:YAG	532	
Nd:YVO <sub>4</sub> diode	532	

Table 1. Lasers used as light source in Raman spectroscopy.

In addition, in order to enhance the laser quality it is possible to employ a pass-band filter, designed to pass only a certain band of frequencies while attenuating all signals outside this band. This component is commonly known as interferometric filter.

2. *Sample illumination system and collection optics*: The collimation and focusing optics of the exciting radiation onto the sample depends on the experimental setup. In principle, excitation

<sup>2</sup> Raman systems are subdivided into two principals according to the spectral analysis of the Raman light, namely Fourier-transform (FT) systems using an interferometer, and dispersive systems.

and collection from the sample can be accomplished in any geometry, although 90 and 180°C (backscattering) are more frequently employed. The use of fiber optics helps to make the spectrometers more versatile.

3. Wavelength selectors and/or separators: The separation or removal of the intense Rayleigh scattering can be achieved by using two different types of filters: notch and edge filters. Notch filters allow the acquisition of the anti-Stokes and Stokes Raman spectra down to ~30 cm<sup>-1</sup>, but their use is expensive since they must be replaced very frequently (~2 years). For this reason, the use of edge filters is widespread. These are wide pass-band filters, which imply that the anti-Stokes Raman spectrum cannot be obtained and typical minimum wavenumbers are ~50 cm<sup>-1</sup>. After the removal or suppression of the Rayleigh radiation, the separation of the different Raman radiations scattered by the sample should be performed. The first Raman spectrometers used prisms, but nowadays these are replaced by gratings that are typically holographically produced. It is worth noting that filters can be neglected if coupling of two or three monochromators is set in a series. This configuration allows not only to separate the Raman lines but also to remove the Rayleigh scatter.

4. *Detectors:* Just like in other spectrometers, the former detectors, that is, photographic films, were substituted first by photodiode array detectors and then by charge transfer devices (CTDs) such as charge-coupled devices (CCDs). CCDs are silicon-based semiconductors arranged as an array of photosensitive elements, each one generating photoelectrons and storing them as an electrical charge. Charges are stored on each individual pixel as a function of the number of photons striking that pixel and then read by an analog-to-digital converter [54].

A schematic representation of a modern micro-Raman spectrometer is shown in Figure 4.



Figure 4. Descriptive scheme of the main components of a Raman microspectrometer.

In the micro-Raman technique, a microscope is integrated in a conventional Raman spectrometer, enabling both visual and spectroscopic measurements. As can be seen in **Figure 4**, in these types of equipment the focusing and collection optics of the scattered radiation are identical. In addition to the analysis of a single point, these spectrometers allow mapping and imaging measurements.

## 3. Results

As explained before, this section has been divided into two parts corresponding to dry and wet conditions; into the corresponding part the developed methods and the results obtained for analogs of the spent nuclear fuel matrix and its alteration products are shown. Namely, the materials studied in this section are the different uranium oxides,  $UO_{2+x}$  (0 < x < 0.25),  $U_4O_9/U_3O_{7,}$  and  $U_3O_{8,}$  and several secondary phases such as rutherfordine, soddyite, uranophane alpha, and kasolite.

The results shown in this section have been obtained by using the LabRaman HR Evolution (Horiba Jobin Yvon Technology, i.e., a dispersive spectrometer equipped with a microscope that enables the unification of both focusing and collection optics. It is possible to couple any laser to the spectrometer optical system as the excitation source. We specifically use the internal HeNe laser of 20-mW nominal power and an excitation wavelength of 632.8 nm (red). The laser beam is focused on the sample through a confocal microscope with different magnifications (5×, 20×, 50×, and 100×). Scattered radiation is then collected by the microscope on its way back (180° scattering) and the Rayleigh contribution removed by an edge filter that cuts at <50 cm<sup>-1</sup>. Thereafter, the Raman-scattered radiation is registered in a Peltier-cooled CCD of 1024 × 256 pixels after crossing a diffraction grating which disperses the signal into its constituent parts. Three gratings of 600, 1800, and 2400 grooves/mm can be selected. The spectral resolution of each grating is ~1, 0.5, and 0.25 cm<sup>-1</sup>/pixel, respectively. The microscope holds a motorized platen in order to carry out both point-to-point and image-scanning spectra, with a 0.1-µm resolution.

In addition to the abovementioned components, different lenses and mirrors can be found throughout the whole optical path, whose function is to correctly direct the beam within the optical system. Due to the amount of components that the laser beam encounters along its way before reaching the sample, a consequent power reduction of around 50% takes place. Nevertheless, the power attained at the sample surface is still sufficient to properly carry out the experiments.

The sample optical image and the spectra acquisition/visualization are performed by means of specific software designed by Horiba. The acquisition parameters and data processing of each spectrum depend on the sample and, above all, on the aim of the study.

#### 3.1. Characterization of different uranium oxides

Here, a methodology to characterize uranium oxide powder with different oxidation degrees is described, and the spectra of stoichiometric UO<sub>2</sub>, hyperstoichiometric UO<sub>2+x</sub>, (0 < x < 0.25),

 $U_4O_9/U_3O_7$ , and finally  $U_3O_8$  have been shown. The sample preparation for obtaining these uranium oxides with different stoichiometry is based on the TGA technique and described in detail elsewhere.

The protocol used to analyze any uranium oxide powder can be summarized in the following steps:

1. Sample visualization: A small amount of uranium oxide is spread over the surface of a microscope slice, which is housed in the stage of the microscope. By using different objectives, we visualize the particles that compound the uranium oxide powder. The microscope digital camera allows us to get optical image of the sample, such as the images shown in **Figure 5**. As can be seen, the powder is finely divided in particles of a size of ~10–20  $\mu$ m.



Figure 5. Optical image of UO<sub>2</sub> powder, acquired with the 5×, 20×, and 100× microscope objectives (from left to right).



Figure 6. Raman spectra acquired as laser power is increased (for the same acquisition times).

2. Setting the acquisition conditions: All spectra are acquired using the laser with an excitation wavelength of 632.8 nm and the 600-grooves/mm grating, thus obtaining a spectral resolution of ~1 cm<sup>-1</sup>/pixel (see *Micro-Raman spectrometer set-up* section). The laser beam is focused on the sample through the 100× magnification objective. Due to the fact that lasers can induce a local temperature increase by up to several hundred degrees if they are focused on a small spot, it

is crucial to check the stability of the sample at high temperature; otherwise, the laser can damage it. In order to do that, a previous study of the sample behavior at different laser powers needs to be done. In this way, **Figure 6** shows the spectra obtained as increasing the laser power, for an acquisition time of 10 min. As can be observed, the sample is stable up to 2 mW for such acquisition time, and then it is burnt from that power on. Therefore, when carrying out the uranium oxide powder characterization experiments, the laser power is minimized to 1 mW in order to ensure that there is no sample alteration during the measurements.



Figure 7. Raman spectra acquired by the multipoint sampling method, in order to check homogeneity of the sample.

3. *Checking the sample homogeneity*: Since the Raman laser excites only a very small portion of the sample (few microns), its homogeneity becomes a critical issue. Therefore, in order to check the sample homogeneity several spectra of different particles are acquired and compared. For obtaining these spectra, the multipoint sampling method is employed. This method uses sequential sample movement and spectrum acquisition, repeated as many times as desired, that is, the motorized *XY* microscope stage is moved to the position in which each spectrum is acquired. **Figure 7** shows the Raman spectra of different particles of a uranium dioxide sample. It can be appreciated that all spectra are similar, indicating that the sample is very homogeneous.

4. *Spectra acquisition*: Once the sample homogeneity is checked, and in order to enhance the intensity/noise ratio all spectra are added. In **Figure 8**, the sum spectrum is shown.

5. Spectra analysis: The aim of the Raman spectra analysis is to obtain information about the frequency, intensity, width, and area of their bands; for this purpose, it is necessary to previously know the number of bands or contributions in the spectrum. One way to detect such contributions is to calculate the spectrum second derivative. This method allows us, first, to determine the number of contributions, since each will lead to a minimum, and, second, to accurately approximate the Raman frequency band center from the position of this minimum.

As an example, the second derivative of the uranium oxide sum spectrum is shown in **Figure 10**. Once the number of contributions of each band is estimated, a Lorentzian fit is conducted using the obtained frequency values as fixed parameters. **Figure 8** also shows the profile analysis of the sum spectrum, where four bands are detected at ~445, 560, 630, and 1150 cm<sup>-1</sup>.

 $UO_2$  presents a fluorite-type structure (fcc), where uranium cations are located at the cubiccoordinated sites and oxygen anions at the tetrahedral-coordinated ones. As oxidation takes place, excess oxygen occupies interstitial positions thus leading to hyperstoichiometric  $UO_{2+x}$ [57]. The crystal system remains cubic up to x = 0.25, known as  $U_4O_9$  [58]. Further oxidation causes the transformation from cubic to tetragonal structure ( $U_3O_7$ ) [59] and finally to orthorhombic ( $U_3O_8$ ).



**Figure 8.** Raman spectrum of uranium oxide powder, corresponding to the sum of several spectra acquired at distinct points of the sample, and its profile analysis (up), and second derivative of such sum Raman spectrum (down).

Since the space group corresponding to uranium dioxide is Fm3m [60], group theory predicts two vibrational modes for UO<sub>2</sub>: a Raman active mode ( $T_{2g}$ ) and an infrared active mode ( $T_{1u}$ ). In such a way, the Raman spectrum of stoichiometric UO<sub>2</sub> presents a band at ~445 cm<sup>-1</sup> assigned to the mentioned  $T_{2g}$  vibrational mode [61]. Likewise, another band at ~1150 cm<sup>-1</sup> is observed, which has been attributed to the 2LO phonon [62]. With regard to the characteristic spectrum of UO<sub>2+x</sub>, it features the same two bands as the stoichiometric oxide, but also an additional broad band located at 500–700 cm<sup>-1</sup> [63]. The same broad band is detected for U<sub>4</sub>O<sub>9</sub> and U<sub>3</sub>O<sub>7</sub>, with a much greater contribution; besides, the 1150 cm<sup>-1</sup> band completely disappears in these oxide spectra [64]. Since U<sub>4</sub>O<sub>9</sub> and U<sub>3</sub>O<sub>7</sub> spectra are similar, it is difficult to distinguish one from each other. Moreover, due to the change to the orthorhombic structure, a widely different spectroscopic profile is obtained for U<sub>3</sub>O<sub>8</sub> [65]. By following the protocol described above, spectra corresponding to uranium oxide powder samples with different sequential oxidation degrees have been obtained:  $UO_{2+x}$  (0 < *x* < 0.25),  $U_4O_9/U_3O_7$ , and  $U_3O_8$ . Some of these spectra are shown in **Figure 9**. Therefore, the behavior of the uranium dioxide Raman spectrum as the oxidation degree increases can be described by the next features: (1) the apparition of different contribution bands at ~500–700 cm<sup>-1</sup>, typical of the hyperstoichiometric oxides  $UO_{2+x}$  (0 < *x* < 0.25), which are due to the incorporation of oxygen into the cubic structure of  $UO_2$  [66]; (2) the disappearance of the 1150 cm<sup>-1</sup> band, characteristic of  $U_4O_9/U_3O_7$  [67]; and (3) the typical three bands at ~375, 450, and 515 cm<sup>-1</sup> and a band at ~812 cm<sup>-1</sup> corresponding to the structure of  $U_3O_8$  [68, 69].



**Figure 9.** Raman spectra of different uranium oxides, where the bottom spectrum corresponds to the hyperstoichiometric  $UO_{2+x7}$  the middle one to  $U_4O_9/U_3O_7$ , and the top one corresponds to the final  $U_3O_8$ .

#### 3.2. Characterization of secondary phases in natural samples

In this section, we present a method based on Raman spectroscopy that allows us an easy and fast identification of secondary phases formed at nature. Secondary phases are present in nature as rims of corrosion products (typically of one or two centimeters wide) found on weathered uraninite<sup>3</sup> crystals. These structures are known as *gummites* because of the difficulties in distinguishing individual phases. The typical alteration rim around an oxidized uraninite crystal, as was described by Frondel [70, 71], is schematically shown in **Figure 10**.

The ore is composed by the uraninite, usually brown to dark brown depending on its oxidation state. Zone 1 contains domains of uranyl oxide hydrates: fourmarierite vandendriesscheite, wölsendorfite, calciouranoite, clarkeite, becquerelite, curite, and schoepite, whereas zone 2

<sup>3</sup> Mineral composed by uranium dioxide, UO<sub>2</sub>, sometimes with small amounts of thorium, therefore with variable formula (U,Th)O<sub>2</sub> (http://www.minerals.net/mineral/uraninite.aspx#sthash.aTasdt1U.dpuf).

consists most commonly of uranyl silicates: uranophane, kasolite, sklodowskite, and soddyite. Anyhow, as expected, the specific alteration products depend on local conditions [72].



Figure 10. Scheme corresponding to the alteration rim of an oxidized uraninite crystal, as described by Frondel.

As an example of how to use Raman spectroscopy to analyze this kind of samples, we show below the characterization of a gummite sample collected in 1960 from Sierra Albarrana (Córdoba, Spain). More details of this study can be found in Ref. [73]. The surface of a polished section of the sample was analyzed by acquiring different spectra along a 10-mm line from the center outwards, in order to know the alteration products sequence (see **Figure 11**).



**Figure 11.** Scheme of the 10-mm line along which different spectra were acquired from the center of the oxidized uraninite crystal outwards.

A combination of the line-mapping and step-by-step procedures can be used to acquire the spectra in this kind of samples. Specifically, in this study a line mapping is performed using the automatized line-scanning tool. This tool allows Raman spectra acquisition of different sample points along a line by automatically moving the stage in one or two directions (*X*-*Y*). The microscope objective used with a magnification of 20× allows the visualization of a maximum  $500 \times 70$ -µm area. Therefore, in order to analyze the whole sample (10 mm), 20 lines with five equidistant points each have been measured, thus acquiring 100 spectra. This was performed with the step-by-step procedure, in which the motorized stage is moved 500 µm (the line-mapping length) in the *x*-direction to allow the analysis of the next part of the sample. The acquisition time for each spectrum was 100 s on an extended shift of 100–1200 cm<sup>-1</sup>. A typical spectrum acquired in this way is shown in **Figure 12**. This spectrum is the characteristic of a mixture of U-minerals that contain uranyl groups in their structure.



**Figure 12.** Typical Raman spectrum acquired during the step-by-step and line-mapping combination procedure. The inset shows the frequency range corresponding to the  $v_1$  symmetric stretch.

It has been demonstrated that the symmetrical-stretching vibration of  $UO_2^{2+}$  can be used as a fingerprint to identify each U-mineral phase [74].  $UO_2^{2+}$  presents a linear symmetry which corresponds to the punctual group  $D_{\infty h}$ . It has four normal modes (3 N – 5, N = number of atoms) and three fundamental vibrations: the symmetric-stretching vibration  $v_1$ , the doubly degenerate bending vibration  $v_2(\delta)$ , and the anti-symmetric-stretching vibration  $v_3$  (see **Table 2**).

Fundamental mode	Vibration	Activity	Infrared frequency (cm <sup>-1</sup> )
v <sub>1</sub>	Symmetric stretch	R	700–900
$\nu_2(\delta)$	Bending	IR	200–300
ν <sub>3</sub>	Anti-symmetric stretch	IR	850–1000

**Table 2.** Normal modes of  $UO_2^{2+}$ .

Although the perfect linear structure has only a  $\nu_1$  Raman active vibration mode, symmetry lowering ( $C_{\omega h} \rightarrow C_{\omega v} \rightarrow C_{2v} \rightarrow C_s$ ) leads to Raman activation of the two IR bands, as well as their overtones and combination vibrations. Moreover, the frequency of each active band is sensible to the environment in which the uranyl group is housed; therefore, each U-mineral has a characteristic  $\nu_1$  symmetric-stretching vibration frequency, which can be used as a fingerprint.

$\overline{\nu_{1}}$ (cm <sup>-1</sup> )	Phase
768	Kasolite
798	Uranophane
832	Soddyite
889	Rutherfordine

Table 3. Characteristic frequencies of the found U-minerals.

In the inset of **Figure 12**, we show the frequency range corresponding to the  $v_1$  symmetric stretch, from 700 to 900 cm<sup>-1</sup>. As can be seen, there are four bands in this region. This must be due to a mixture of four different phases, if we understand the Raman spectra for mixtures as the direct sum of the individual spectrum of each component in the mixture (as long as these components do not interact with each other). Therefore, in this kind of mixtures the vibration bands do not undergo any displacement, and the band profile of the mixture spectrum results in the spectra of the different components or vice versa.

Taking this into account, the characteristic frequency bands observed in **Figure 12** correspond to the following U-minerals: rutherfordine,  $UO_2(CO_3)$ , uranophane alpha,  $Ca(UO_2)_2(SiO_3OH)_2$  5H<sub>2</sub>O, soddyite,  $(UO_2)_2SiO_2$  2H<sub>2</sub>O, and kasolite, PbUO<sub>2</sub>SiO<sub>4</sub>H<sub>2</sub>O (see **Table 3**). See Refs. [75–78] for the assignments.

Position	Min. at 768 cm <sup>-1</sup>	Min. at 798 cm <sup>-1</sup>	Min. at 832 cm <sup>-1</sup>	Min. at 889 cm <sup>-1</sup>
(mm)	(kasolite)	(uranophane)	(soddyite)	(rutherfordine)
0	No	No	No	No
0.9 mm	No	No	Yes	Yes
3.7 µm	No	Yes	Yes	No
9.1 mm	Yes	Yes	No	No

Table 4. Result data matrix.

In order to perform a semi-quantitative analysis of the sample with the aim of detection of different phases along the sample, next spectra processing has been carried out:

(i) Second-derivative calculation in the  $v_1$  region (700–900 cm<sup>-1</sup>).

(ii) Verification of the existence of a minimum at each characteristic frequency.

(iii) Construction of a data matrix of 0 and 1, where 0 means there is no minimum at the characteristic frequency of the mineral and 1 means there is such a minimum (see **Table 4**).

This data matrix enables constructing different diagrams. As an example, in **Figure 13** we present a scheme where the existence or absence of each phase at each position can be appreciated only by looking at the minimum of the second-derivative spectrum.



Figure 13. Sequence of the urananite alteration products.

As can be seen, the sequence of alteration products obtained was as follows: (1) uraninite constitutes the unaltered core of the sample, 0–0.4 mm. (2) Rutherfordine appears in the inner part, 0.4–3.3 mm, in contact with the uraninite core. (3) Then, a mixture of uranyl silicates, soddyite, uranophane alpha, and kasolite is found. Soddyite prevails in the inner part, 0.4–7.1 mm; uranophane alpha predominates in the outer part of the sample, 7.1–10 mm, and kasolite appears intermittently (1.0–3.3, 4.6–7.1, and 8.8–10 mm).

## Author details

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### References

- [1] Nuclear Safety Review 2015, IAEA/NSR/2015, IAEA, Austria, 2015.
- [2] Organisation for economic co-operation and development (OECD) annual report, 2002. DOI: 10.1787/annrep-2002-en.
- [3] Rodriguez Villagra N. Fuel stability of Th / Pu / MOX at disposal conditions [thesis]. Universidad Complutense de Madrid; 2015. ISBN: 978-84-7834-739-1.
- [4] Zakaria M. Atoms for Peace? Nuclear Energy and Peace. Bachelor thesis (C-essay) Peace and Conflict Studies (PACS) [thesis]. Faculty of International Migration and Ethnic Relations (IMER); 2006.
- [5] de Groot JI, Steg L, Poortinga W. Risk Analysis. 2013;33:2:307–317. DOI: 10.1111/j.1539.
- [6] Ahokas J. The role of nuclear power in the future energy system [thesis]. University of LUT School of Technology; 2015.
- [7] Jung-Chun H, Chiao-Tzu P, Shu-Fen K, Ruey-Yu C, Leonga M, Hung-Lun C, Wan-Hua H, Chun-Chiao T, Cheng-Fung L, Suei-Loong L. Environment International. 2014;73:295–303.
- [8] OECD/IEA Technology Roadmap: Nuclear Energy. [Internet]. 2015. Available from: http://www.iea.org/t&c/termsandconditions/
- [9] Choppin G, Liljenzin JO, Rydberg J. Radiochemistry and Nuclear Chemistry, Reed Educational and Professional Publishing Ltd., Oxford; 1995.
- [10] Astudillo Pastor J. El almacenamiento geológico profundo de los residuos radiactivos de alta actividad: principios básicos y tecnología. Editorial: Madrid: ENRESA, D.L; 2001.
- [11] Kleykamp H. Journal of Nuclear Materials. 2004;131:221–246.
- [12] Buck EC, Hanson BD, McNamara BK. The Geological Society of London Special Publication. 2004;236:65–88.
- [13] Shoesmith DW. Journal of Nuclear Materials. 2000;282:1–31.
- [14] Bruno J, Ewing RC. Elements. 2006;2:343–349.
- [15] Hedin A. Spent Nuclear Fuel—How Dangerous Is It? SKB Technical Report 97-13, Swedish Nuclear Fuel and Waste Management Co.; 1997, 60 pp.
- [16] de Saillan C. Harvard Environmental Law Review. 2010;34:461–519.
- [17] Nimander F. Investigation of Spent Nuclear Fuel Pool Coolability, Division of Nuclear Reactor Technology Royal Institute of Technology, Stockholm; 2011.
- [18] McEachern RJ, Taylor P. Journal of Nuclear Materials. 1998;254:87–121.

- [19] SKB 91. Final Disposal of Spent Nuclear Fuel. Importance of the Bedrock for Safety, SKB Report 92-20; May 1992.
- [20] Geological Disposal of Radioactive Waste: Technological Implications for Retrievability. IAEA TR No. NW-T-1.19, 2009. ISBN 978-92-0-100109-2.
- [21] Olander DR. Fundamental Aspects of Nuclear Reactor Fuel Elements, Technical Information Center, Office of Public Affairs-Energy Research and Development Administration; 1976, ISBN 0870790315, 9780870790317, 613 pp.
- [22] Meredith S., Coonley IM-1, David L. Clark, Gordon D. Jarvinen. Eds. Actinide Oxides, Actinide Research Quarterly, Los Alamos Laboratory, Annual Report 2004. Nuclear Materials Research and Technology.
- [23] Belle J, Ed. Uranium Dioxide: Properties and Nuclear Applications, Naval Reactors, Division of Reactor Development, USAEC; 1961.
- [24] SKB-91. Final Disposal of Spent Nuclear Fuel. Importance of the Bedrock for Safety. Report 92-20; May 1992.
- [25] Ewing RC. Nature Materials. 2015;14:252–257.
- [26] Shoesmith DW. Journal of Nuclear Materials. 2000;282:1–31.
- [27] Sunder S. Nuclear Technology. 1998;122:211–221.
- [28] Christensen H, Sunder S. Journal of Nuclear Materials. 1996;238:70–77.
- [29] Roth O, Jonsson M. Central European Journal of Chemistry. 2008;6:1–14.
- [30] Amme M, Renker B, Schmid B, Feth MP, Bertagnolli H, Döbelin W. Journal of Nuclear Materials. 2002;306:202–212.
- [31] Rey A, Giménez J, Casas I, Clarens F, Pablo J. de. Applied Geochemistry. 2008;23:2249– 2255.
- [32] Lousada CM, Trummer M, Jonsson M. Journal of Nuclear Materials. 2013;434:434–439.
- [33] Frondel C. American Mineralogy. 1956;4:539–568.
- [34] Plasil J. Journal of Geoscience. 2014;59:99–114.
- [35] Musolino SV, DeFranco J, Schlueck R. The Radiation Safety Journal. Health Physics. 2008;94(2):109–111. DOI: 10.1097/01.HP.0000285801.87304.3f.
- [36] Guimbretière G, Desgranges L, Jegou C, Canizarès A, Simon P, Caraballo R, Raimboux N, Barthe MF, Ammar MR, Maslova OA, Duval F, Omnée R. IEEE Transactions on Nuclear Science. 2014;61:2045.
- [37] Guimbretière G, Canizares A, Simon P, Tobon-Correa YA, Ammar MR, Corbel C, Barthe MF. Spectroscopic Letters. 2011;44:570.

- [38] Jégou C, Caraballo R, Bonfils J de, Broudic V, Peuget S, Vercouter T, Roudil D. Journal of Nuclear Materials. 2010;399:68.
- [39] Jégou C, Caraballo R, Peuget S, Roudil D, Desgranges L, Magnin M. Journal of Nuclear Materials. 2010;405:235.
- [40] Sarsfield MJ, Taylor RJ, Puxley C, Steele HM. Journal of Nuclear Materials. 2012;427:333.
- [41] Desgranges L, Pontillon Y, Matheron P, Marcet M, Simon P, Guimbretière G, Porcher F. Inorganic Chemistry. 2012;51:9147.
- [42] Böhler R, Çakır P, Beneš O, Hein H, Konings RJM, Manara D. The Journal of Chemical Thermodynamics. 2015;81:245.
- [43] Böhler R, Quaini A, Capriotti L, Çakır P, Beneš O, Boboridis K, Guiot A, Luzzi L, Konings RJM, Manara D. Journal of Alloys and Compounds. 2014;616:5.
- [44] Böhler R, Welland MJ, Prieur D, Cakir P, Vitova T, Pruessmann T, Pidchenko I, Hennig C, Guéneau C, Konings RJM, Manara D. Journal of Nuclear Materials. 2014:448:330.
- [45] Naji M, Colle JY, Beneš O, Sierig M, Rautio J, Lajarge P, Manara D. Journal of Raman Spectroscopy. 2015;46,750–756.
- [46] Casas I, Giménez J, Martí V, Torrero ME, de Pablo J. Radiochimica Acta. 1994;66:23–27.
- [47] Fors P, Carbol P, Van Winckel S, Spahiu K. Journal of Nuclear Materials. 2009;394:1–8.
- [48] Bruno J, Casas I, Sandino MCA. Journal of Nuclear Materials. 1992;190:61–69.
- [49] Ollila K. Journal of Nuclear Materials. 1992;190:70–77.
- [50] Raman CV, Krishnan KS. Nature. 1928;121:501–502.
- [51] Beran A, Lobowitzky U. EMU Notes in Mineralogy. Eötvös University Press; 2004.
- [52] Hollas JM. Modern Spectroscopy. John Wiley & Son Ltd.; 2004.
- [53] Long DA, Raman Spectroscopy, McGraw-Hill International Book Company; 1977.
- [54] Willes W, Merlin R. Eds. Raman Scattering in Materials. Springer Series in Materials Science, Vol. 42. Springer-Verlag, Berlin; 2000.
- [55] Lewis IR, Edwards H. Handbook of Raman Spectroscopy: From the Research Laboratory to the Process Line. Practical Spectroscopy Series, Vol. 28, CRC Press, Boca Raton, FL, USA; 2001.
- [56] Egyptian Journal of Forensic Sciences. 2015. Available from: http://dx.doi.org/10.1016/ j.ejfs.2015.06.001
- [57] Willis BTM. Acta Crystallographic.1978;34:88–90.
- [58] Hering H, Perio P. Bulletin de la Societe Chimique. 1952;351.
- [59] Jolibois P. Comptes Rendus de l'Academie des Sciences, Paris. 1947; 224:1395.

- [60] Graves PR. Applied Spectroscopy. 1990;144:1665.
- [61] Marlow PG, Russell JP, Hardy JR. Philosophical Magazine. 1966;14:409.
- [62] Livneh T, Sterer E. Physical Review B. 2006;73:085118–085119.
- [63] He H, Shoesmith D. Physical Chemistry Chemical Physics. 2010;12:8108.
- [64] Manara D, Renker B. Journal of Nuclear Materials. 2003;321:233–237.
- [65] Allen C, Butler S, Tuan NA. Journal of Nuclear Materials. 1987;144:17–19.
- [66] Manara D, Renker B. Journal of Nuclear Materials. 2003;321:233–237.
- [67] Desgranges L, Baldinozzi G, Simon P, Guimbretière G, Canizares A. Journal of Raman Spectroscopy. 2012;43:455–458.
- [68] Allen GC, Butler IS, Tuan NA. Journal of Nuclear Materials. 1987;144:17–19.
- [69] Palacios ML, Taylor SH. Applied Spectroscopy. 2000;54:1372.
- [70] Frondel C. US Geological Survey Bulletin. 1958;1064.
- [71] Frondel C. American Mineralogy. 1956;41:539–568.
- [72] Robert F, Rodney E. Uraninite alteration in an oxidizing environment and its relevance to the disposal of spent nuclear fuel; SKB Technical Report 91-15; 1990.
- [73] Bonales LJ, Menor-Salván C, Cobos J. Journal of Nuclear Materials. 2015;462:296–303.
- [74] Frost RL, Čejka J, Weier M, Wayde M. Journal of Raman Spectroscopy. 2006;37(9):879– 891.
- [75] Frost RL, Jiri C. Journal of Raman Spectroscopy. 2009;40:1096–1103.
- [76] Rost RL, Cejka J, Weier ML, Martens W. Journal of Raman Spectroscopy. 2006;37:538– 551.
- [77] Frost RL, Weier ML, Martens W, Kloprogge T, Cejka J. Spectrochimica Acta. 2006;63:305–312.
- [78] Biwer BM, Ebert WL, Bates JK. Journal of Nuclear Materials. 1990;175:188–193.