



## Recognition of uranium oxides in soil particulate matter by means of $\mu$ -Raman spectrometry

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### ABSTRACT

Soil samples from an abandoned uranium mine have been investigated in order to determine the molecular phases of uranium compounds. The experiments were carried out with soil particulate matter, collected randomly from the area of the formerly exploited ore. To select the particles rich with uranium, scanning electron microscopy with energy-dispersive X-ray attachment (SEM/EDX) was applied first. Afterwards, the particles were relocated and measured by  $\mu$ -Raman spectrometry (MRS). Residues of the main deposit, uraninite  $\text{UO}_2$ , were detected, along with its alteration products. In terms of Raman scattering properties, uranium oxides are quite sensitive to the laser beam wavelength, which results in very specific features of their Raman spectra. In this paper the Raman spectra of uranium oxides of different origin and oxidation states, measured with 514 and 785 nm lasers, are also presented.

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### 1. Introduction

The recognition of uranium oxides with the help of  $\mu$ -Raman spectrometry (MRS) is a task of great importance for at least two reasons. First off, all U compounds will always be of interest due to their strategic role in the world-wide economy; the knowledge about their origin, location, alteration, speciation, as well as their impact on human health and environment is of great importance. Secondly, the application of MRS enables in a fast and presumably non-destructive way to determine the molecular composition and to distinguish forms of various oxidation states.

The molecular structure of U oxides has been a goal of several studies during the last few years and still remains attractive because of their numerous complex phases and the transformations they go through. It is noticeable that a number of discrepancies have appeared so far in the open literature, especially when interpretation of the resulting Raman spectra is still ambiguous [1–9]. The reason for this uncertainty might be settled in the nature of U–O compounds because they tend to get non-stoichiometric by incorporating additional oxygen atoms [1]. Moreover, these compounds are reported to be sensitive to the excitation wavelength

[2] and susceptible to alteration (i.e. oxidation) under the laser beam. A survey through the open literature showed many data regarding Raman fingerprints of various U–O phases and the band positions reported by authors are not always consistent with one another. The summary is presented in Table 1.

Obviously, U dioxide is the most often examined compound, with two characteristic bands: 445 (446) and 1150 (1151)  $\text{cm}^{-1}$ . They are typical for stoichiometric  $\text{UO}_2$ . The first one, mainly presented at 445  $\text{cm}^{-1}$ , is ascribed to a stretching mode of U–O bond. The latter one (at 1150  $\text{cm}^{-1}$ ) is attributed to crystal field perturbations instead of the typical scattering. That does not exhaust the subject, since there are many other shifts reported (see Table 1), sometimes difficult to be interpreted. According to Graves [3], the numerous measurements of single  $\text{UO}_2$  crystals showed the presence of four bands (Table 1), the feature at 630  $\text{cm}^{-1}$  being reported as not interpretable. An additional feature observed (575  $\text{cm}^{-1}$ ) in the  $\text{UO}_2$  spectrum, after implantation of Kr ions into the  $\text{UO}_2$  lattice, was ascribed to a damaged crystal matrix. A similar interpretation was presented by Senanayake et al. [2], who observed also an extra feature at 585  $\text{cm}^{-1}$  in the spectrum of  $\text{UO}_2$ . Manara and Renker [5] reported a presence of the band 232  $\text{cm}^{-1}$  ( $237 \pm 5$ ), which origin was not fully clear. Additional bands might occur in the Raman spectrum with the change of the excitation wavelength [2], as it may be seen in Table 1.

The reason of all discrepancies and difficulties in the shape of Raman spectra of U–O system might be explained by its fast and

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**Table 1**  
Summary of Raman spectra of U oxides, presented in the literature

Formula	Laser (nm)	Raman shift bands (cm <sup>-1</sup> )	Reference
UO <sub>2</sub>	514	445	[1]
	514	448, 630, 1104, 1152	[3]
	514	445	[4]
	514	232, 445, 1151	[5]
	488	450, 585, 1595 (1150 + 445)	[2]
	488	445, 585, 920, 1150*	[2]
Uraninite	785	445, 583, 640, 1160, 1360*	[2]
	1064	369, 445	[9]
U <sub>4</sub> O <sub>9</sub>		210, 465	[7]
U <sub>3</sub> O <sub>7</sub>		210, 465	[7]
		410, 445, 500	[4]
U <sub>3</sub> O <sub>8</sub>	514	343, 351, 412, 483, 738, 811	[1]
	514	236, 342, 408, 480, 752, 798	[4]
	488	235, 340, 405, 480, 640, 745, 800, 885	[2]
	514	236, 342, 408, 480, 638, 752, 798, 888	[8]
γ-UO <sub>3</sub>	514	768, 846	[1]
Schoepite	1064	843, 845 (double peak)	[9]
UO <sub>2</sub> (OH) <sub>2</sub>		838, 855	[15]

\* Single crystal measurement.

easy oxidation under the laser beam. The process of the phase change via an increase of the oxidation state of U was also a topic of numerous researches. Senanayake et al. [2] observed the visual changes on the UO<sub>2</sub> surface exposed to water vapors; owing to MRS the product of the surface reaction was proven to be U<sub>3</sub>O<sub>8</sub> due to the growing intensity of 240, 405 and 756 cm<sup>-1</sup> band. A transformation from UO<sub>2</sub> to U<sub>3</sub>O<sub>8</sub> goes through a displacement of lattice oxygen atoms from their ideal position and incorporating additional oxygen atoms, followed by a distortion of a crystal structure, which was reported by Allen and co-workers [6]. They presented a spectrum of powdered UO<sub>2</sub> exposed to a laser beam that also confirmed acceleration of the oxidation process. As it goes from UO<sub>2</sub> through U<sub>4</sub>O<sub>9</sub> and U<sub>3</sub>O<sub>7</sub> to U<sub>3</sub>O<sub>8</sub>, the strongest band 445 cm<sup>-1</sup> weakens, splitting finally into two separate bands: 408 and 480 cm<sup>-1</sup>.

Lightly oxidized (freshly polished) and heavily oxidized (2 years ageing) U surface was investigated by Siekhaus [7]. The reaction leads to a formation of a phase with positions: 446, 578, 735, 950 and 1150 cm<sup>-1</sup>. However, 445 and 1150 bands would reveal the presence of UO<sub>2</sub>, the other ones suggest a more complicated phase. As the oxidation proceeds, more features appear within the range 235 and 450 and also 480–810 cm<sup>-1</sup>, showing a variation of U oxides. Manara and Renker [5] were analyzing non-stoichiometric U dioxide, pointing out that UO<sub>2+x</sub> system with 2.09 ≤ O/U ≤ 2.20 is characterized by extra Raman features raising with the increase of oxygen atoms incorporated, such as 237, 335, 410, 475 and 750 cm<sup>-1</sup>. These band positions appear in the U<sub>3</sub>O<sub>8</sub> Raman spectrum according to a majority of researchers (see Table 1). The structure of U<sub>3</sub>O<sub>8</sub> is well described by Butler et al [8]; contrary to the other U–O compounds, it is not sensitive to a laser wavelength.

As seen from the above, the recognition of U-oxide system is not trivial, even in case of pure substances under laboratory conditions. A large number of U–O phases and their changeability, which allows them to get transformed into one another, make their determination quite challenging. The problem becomes complex when we consider disposed nuclear waste or abandoned exploration areas. The main component of directly disposed U (i.e. spent fuel) is UO<sub>2</sub> and its alteration products, depending on the environmental conditions [9]. UO<sub>2</sub>, being also a main source of U, is the most abundant form of U oxide (uraninite). Both UO<sub>2</sub> wastes (nuclear spent fuel) and naturally occurring mineral undergo the transformations to silicates and/or composed oxyhydroxides. The altered material was conclusively distinguished from UO<sub>2</sub> matrix by MRS owing to a precisely built-up spectroscopic library [9]. It is obvious that recognizing of molecular phases occurring in the natural envi-

ronment, especially within the areas of a special concern (as mentioned above), is essential to predict their chemical properties, mobility, solubility, reactivity etc. The presence of U oxides and their transformation products in the shape of particulate matter only extends their hazardous nature due to an additional chance to spread around.

Searching for U-rich particles and recognition of its species in single, separated particles was a task of the investigations described in this paper. The particles came from the U ore located in the south part of Hungary, at the foot of the Mecsek Mountains, close to the town of Pecs. Exploration of the ore was carried out since 1953 till 1997, when the production of U was shut down by the government. During the whole period of mining, about 45 million ton of rock has been processed, of which 18 million tons was a waste rock, dumped in 5 waste piles within the mining area [10]. The principal ore-forming minerals of the deposit are pitchblende in various oxidation states between UO<sub>2</sub> and UO<sub>3</sub> and coffinite USiO<sub>4</sub>. The final product of enrichment was so-called 'yellow cake' (U<sub>3</sub>O<sub>8</sub> with impurities) [11].

The experiments were performed within a large scale project to estimate the impact and eventual risk for the environment caused by remains of the formerly explored ore. The main focus was on the examination of molecular composition of U-rich phases occurring in the soil particles. MRS is a very convenient technique to analyze areas of micrometer size due to the enhancement of a Raman spectrometer with a visible light microscope. However, the basis for a successful recognition of U oxides present in environmental soil particles is a rich database, including a whole variety of the binary U–O system. Both synthesized and naturally occurring U oxides were used to extend our spectral library, then the analysis of environmental samples collected in the abandoned deposit site were analysed.

## 2. Experimental

### 2.1. Samples

As reference materials, four compounds were used: (I)UO<sub>2</sub> standard in the form of fine black powder, made in the KFKI laboratory [12,13], (II)U<sub>3</sub>O<sub>8</sub> standard – yellow powder [10], (III)(UO<sub>2</sub>)<sub>8</sub>-O<sub>2</sub>(OH)<sub>12</sub>·12H<sub>2</sub>O – synthesized schoepite, produced from a solution of (UO<sub>2</sub>)(NO<sub>3</sub>)<sub>2</sub> through alkaline hydrolysis and (IV)uraninite – an original sample of ore exploited in the U mine. The phase composition of each reference materials was confirmed by means of X-ray powder diffraction XRPD (Philips model PW 3710 based PW 1050 Bragg-Brentano parafocusing goniometer using Cu Kα radiation (λ = 0.15418 nm), graphite monochromator and proportional counter). The XRD scans were digitally recorded with a step size of 0.04° and evaluated for phase composition with a full profile fitting method.

The samples were collected from different areas of ore exploration. The geological cross section in the western part of the mountains, cut from 2500 m deep to the surface consists of: sandstone (lower permian Korpád Sandstone Formation), rhyolite (lower Permian Gyrf Rhyolite Formation), sandstone (upper Permian Cserdi Sandstone Formation) albitic claystone (upper Permian Boda Siltstone Formation) and sandstone with U ore-bearing sandstone layers (upper Permian Kvgőszls Sandstone Formation) and is covered by sandstone (lower Triassic Jakabhegy Sandstone Formation) and lower and middle siltstone and limestone [14].

### 2.2. Measurements

The collected soil samples were crushed with a plastic rod and sieved through 0.67 μm sieve. They were afterwards deposited on

carbon disks and examined by means of SEM/EDX system to locate U-rich particles. It was performed by a JEOL JSM 6300 Scanning Electron Microscope (JEOL, Tokyo, Japan) equipped with both a backscattered electron detector (BSE) and a secondary electron detector (SE). Additionally, an energy-dispersive X-ray detection system was used. A Si (Li) X-ray detector PGT (Princeton Gamma Tech, Princeton, NJ, USA) was employed for acquiring the X-ray spectra. The acceleration voltage was 30 kV and the spectra were collected for 60 s each at 1 nA current.

Molecular analysis was performed with a Renishaw InVia micro-Raman dispersive system coupled with a Peltier cooled CCD detector. Excitation was provided by both the 514.5 nm Ar laser and 785 nm diode laser. Samples were scanned using a synchroscan mode from 100 to 2000  $\text{cm}^{-1}$  at a spectral resolution of about 2  $\text{cm}^{-1}$ . The acquisition time for each scan varied from 10 to 40 s, to obtain the best condition for the analyzed spot. The number of accumulations varied from 1 to 10 in order to provide a better signal-to-noise ratio. Spectra were obtained using 100 $\times$ , 50 $\times$  or 20 $\times$

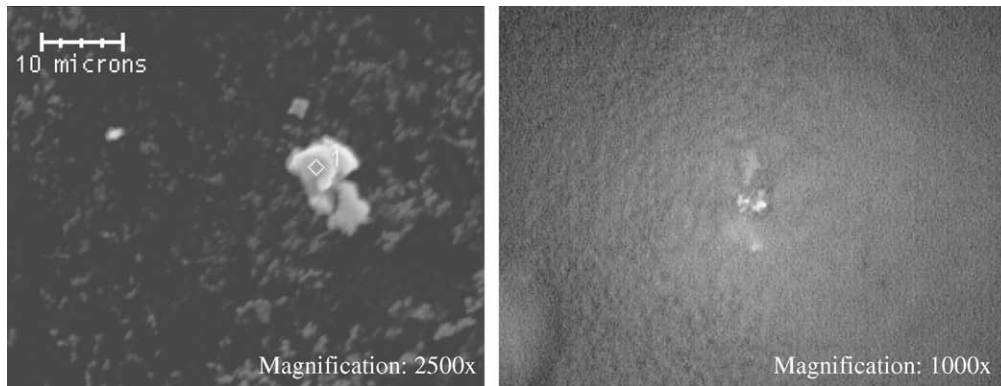


Fig. 1. SEM image (left) and visible light image (right) of the same U-rich particle.

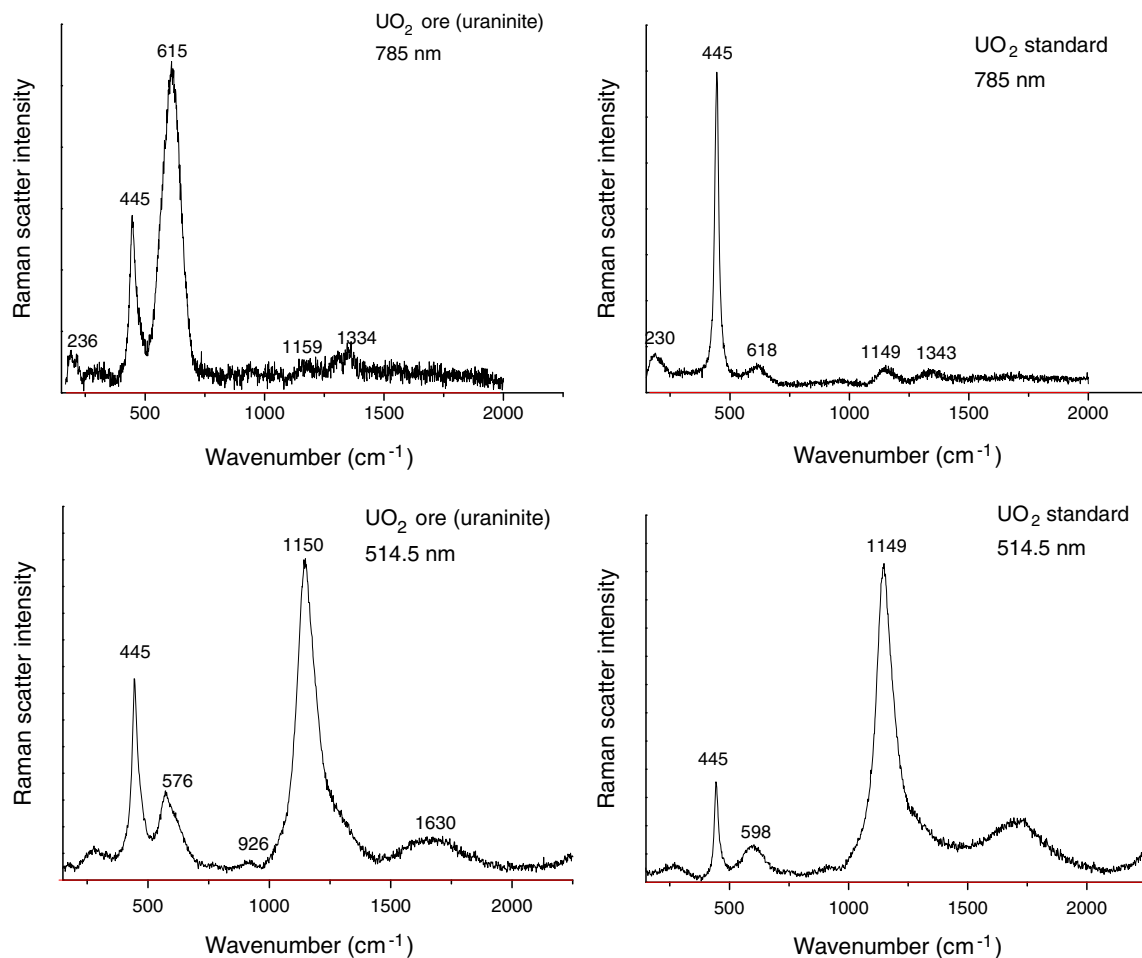


Fig. 2. Raman spectra of  $\text{UO}_2$  of various origin, recorded at different excitation wavelengths.

magnification objectives. Calibration was done using the  $520.5\text{ cm}^{-1}$  line of silicon. Data acquisition was carried out with the Spectralcalc software package GRAMS (Galactic Industries, Salem, NH, USA). Spectral analyses were performed by comparison with spectra from an in-house library as well as a commercially available spectral library.

Subsequent measurements by two stand alone instruments were optimized in order to facilitate collection of both elemental and molecular spectra from the same object. For that reason the soil particles were first analyzed with SEM/EDX to locate and mark the position of U-rich objects. The crucial part was to use raw samples, not coated and not altered, which was possible in case of small particles deposited on a carbon disk. Afterwards the disks were placed in the MRS chamber and the U-rich spots were relocated and analyzed. Fig. 1 presents the two images of the same object – one image comes from the SEM (SE detector), the other is taken with a help of an optical microscope coupled with MRS system. The whole procedure, including also the particles deposition, is described in details elsewhere [15].

### 3. Results and discussion

#### 3.1. Collecting the reference spectra

As it is clearly visible from the literature research,  $\text{UO}_2$  and its alteration products are very sensitive to a wavelength of a laser

used, which is also confirmed hereby. The spectra recorded for the samples used as references are presented in Fig. 2.

All the spectra show the band typical for stoichiometric  $\text{UO}_2$ , appearing at  $445\text{ cm}^{-1}$ , ascribed to a stretching mode of U–O bond. This is the most characteristic feature of the Raman spectrum for a fluorite-like structure of  $\text{UO}_2$ . The other bands, however, require additional attention with respect to their interpretation. The spectra of  $\text{UO}_2$  used as a standard are in a very good agreement with those presented by Senanayake et al. [2]. The accordance is surprisingly good; not only positions, but also relative heights of the peaks are comparable. Also the spectrum recorded with the help of a 785 nm laser (Fig. 2) resembles a lot the one shown in their paper [2], except the band at  $618\text{ cm}^{-1}$ , instead of which there were two observed:  $583$  and  $640\text{ cm}^{-1}$ . The band at  $1150\text{ cm}^{-1}$  was attributed to crystal field perturbation instead of the typical scattering. This feature was observed in some cases (see Table 1).

The spectrum of uraninite is comparable to the standard especially after the excitation with the green 514 nm laser. The spectra obtained at 785 nm are different when comparing the ratio of the two main peaks. Unfortunately, Raman analysis of uraninite is not widely presented in the open literature and even freely available Raman spectra databases do not contain the spectrum of this mineral. Amme et al. [9] analyzed the products of nuclear fuel corrosion and presented the spectra of uraninite and its alteration products. The authors pointed out the two main bands in the Raman spectrum: one typical for all  $\text{UO}_2$  forms at  $445\text{ cm}^{-1}$  and  $369\text{ cm}^{-1}$  of unknown origin. The band at  $615\text{ cm}^{-1}$ , although

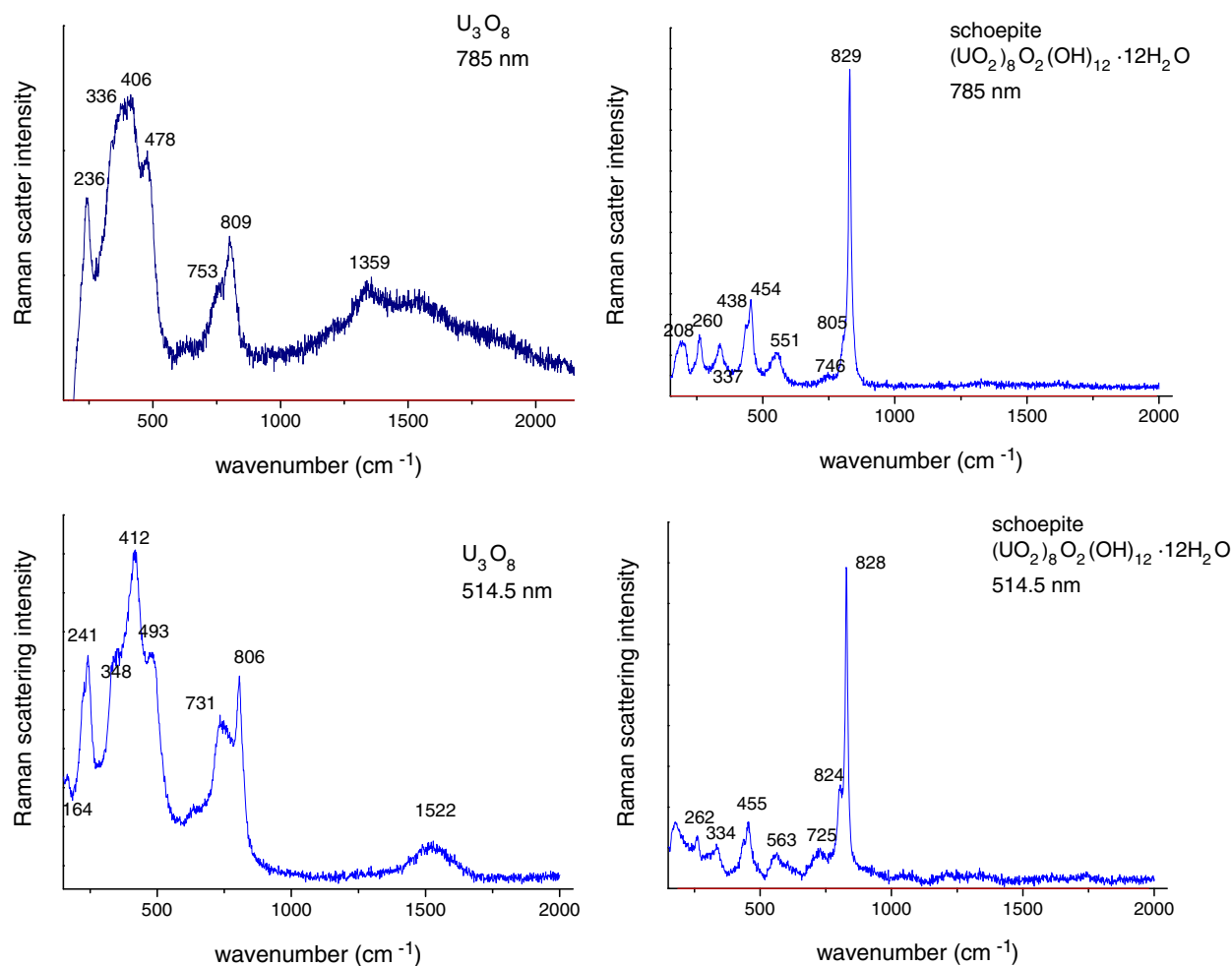


Fig. 3. Raman spectra of other uranium (hydro)oxides recorded at different wavelengths.

visible also in the standard spectrum as a weak and broad peak, is very intensive in this case and its interpretation remains ambiguous.

The other reference spectra are presented in Fig. 3. In case of  $U_3O_8$  the data are in a good agreement with the one given by Palacios and Taylor [1], Allen et al. [4], Manara and Renker [5] and Butler et al [8]. It should be mentioned, however, that excitation with both 785 and 514 lasers induces Raman spectra quite resembling each other, although with a slight shift of the main bands. The second compound, used as a reference, is schoepite ( $UO_2$ )<sub>8</sub>-

$O_2(OH)_{12} \cdot 12H_2O$ . This mineral was reported as a natural alteration product of uraninite [9]. This process goes through oxidation of U(IV) to U(VI) and appearance of highly mobile uranyl ion  $UO_2^{2+}$ . Its Raman activity is well detectable as a shift occurring in the range of 800–900  $cm^{-1}$ , due to its symmetric stretching vibration. According to Amme and co-workers [9], the exact frequency of this mode depends on the Z-number of the other atoms participating in the bond. The shift of the Raman band to higher wavenumbers is observed when the lighter elements appear in the mineral structure. In the same paper they also presented the Raman spectra of

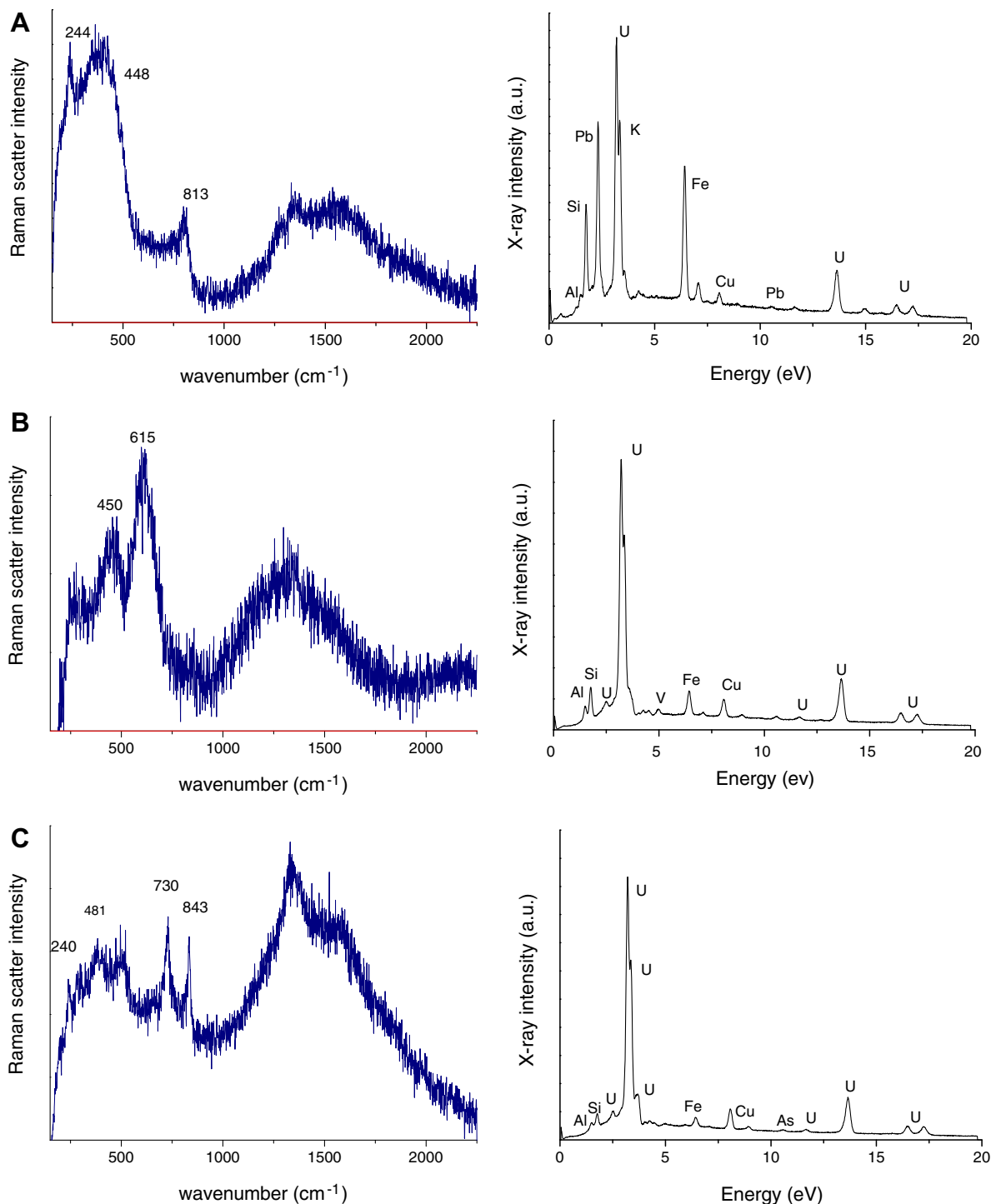


Fig. 4. Combined analysis of particles from the abandoned Hungarian mine – Raman spectra of uranium oxides coupled with adequate SEM/EDX spectra.



synthetic schoepite ( $\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}$ ), also produced through a hydrolysis of uranyl nitrate. They reported a double peak at the frequencies 843/855  $\text{cm}^{-1}$  and also quoted the other values, such as 840/860 [9]. According to Frost and co-authors [16], uranyl stretching bands in the schoepite Raman spectrum appear at 838 and 855  $\text{cm}^{-1}$ . The spectra presented in this paper contain a strong single band at 829 (828)  $\text{cm}^{-1}$ , broadened at its feet by overlapping with another band. Here we can observe some small difference, since an overlapping band appears at 805  $\text{cm}^{-1}$  for the 785 nm excitation wavelength or 824  $\text{cm}^{-1}$  for 514 nm. On the other hand, both spectra of schoepite presented in Fig. 2 look very similar comparing the lower spectral range (100–600  $\text{cm}^{-1}$ ), which proves the less sensitivity of this phase to a laser beam.

### 3.2. Analysis of U-rich particles

In Fig. 4 there are Raman spectra of U-rich particles, found in various spots of the former Hungarian U mine. They were selected by means of SEM/EDX with the help of the BSE image. The collected X-ray spectra showed also the presence of some crustal elements, but U was a major one.

The selected examples represent the majority of U oxide phases detected by MRS. The spectra are very noisy and in the images they were kept in their original forms (not smoothed). The particles with U content were rather small, sometimes being a part of a larger agglomerate. This required extreme diminishing of a laser spot to ca 1  $\mu\text{m}$  size (this refers to a laser of 785 nm; the lower the wavelength, the smaller the spot size [15]). That always goes at the expense of signal intensity and worsens the signal-to-noise ratio. Besides, the problem with Raman analysis of small objects is settled in collecting a very weak Raman signal, which requires a number of accumulations [15], especially when it involves environmental samples, which are heterogeneous by their nature. These particles, beside U-rich phase, contained also a significant amount of organic matter, which probably caused a high fluorescence level (not shown in Fig. 4 for a better presentation of band positions).

A comparison of the spectra shown in Fig. 4 with the reference ones (Figs. 2 and 3) leads to the conclusion that in the area of former mine activity after a break of 10 years,  $\text{UO}_2$  particles got transformed to higher oxidation state such as  $\text{U}_3\text{O}_8$  (Fig. 4(B)), although there were also individuals preserved with a structure of uraninite (Fig. 4(A)). The third example (Fig. 4(C)) is more ambiguous; however its molecular structure suggests the presence of  $\text{UO}_3$  and/or schoepite. The spectrum with two sharp bands at 730 and 843  $\text{cm}^{-1}$  resembles the features typical for U(VI) structure, as it is described elsewhere [1]. It is also confirmed by the yellowish color of this particle. The spectrum shape with typical features within the range 200–500  $\text{cm}^{-1}$  suggests the presence of  $\text{U}_3\text{O}_8$ , but the band at 843  $\text{cm}^{-1}$  would refer to a U(VI) oxidation state. We cannot exclude the mixture of both phases. In case of natural samples this is not exceptional. Mellini and Riccobono [17] described the unidentified U corrosion product, which was the yellow material covering the depleted U dart (ani-tank penetrators used in 1999 in Western Kosovo). The Raman bands of 744 and 812  $\text{cm}^{-1}$  would prove also the presence of U(VI) form, however the U phase was not fully recognized.

These results revealed that in the natural environment of the abandoned U mine, the most thermodynamically stable phases of U–O system, such as  $\text{UO}_2$ ,  $\text{U}_3\text{O}_8$  [2] can be detected. The presence of other U(VI) oxide cannot be excluded, although was not confirmed by the reference samples. Uranium minerals such as schoepite, studite, etc., reported elsewhere [9] as phases appearing due to the natural oxidation of uraninite, were not confirmed. Considering the potential risk that might be caused by the residues of explored U ore for the environment, the recognition of U oxidation state is fundamental and MRS is the suitable technique for this purpose. Bulk analysis, performed also by XRD, confirmed only the presence of uraninite, but the more highly oxidized forms remained unrevealed. Individual particle analysis performed by two micro-techniques made it feasible to recognize all oxidation states of U oxides, collected directly in their natural environment.

### 4. Conclusions

The molecular analysis of selected U–O compounds, performed by MRS, showed a variety of features depending on the origin of the sample and the laser wavelength applied. The stoichiometric  $\text{UO}_2$  appeared very sensitive to the excitation wavelength, since, beside of the most characteristic band at 445  $\text{cm}^{-1}$ , the spectra contained numerous minor bands of various positions and intensities. It is therefore essential to build up a spectral library which facilitates correct recognizing of molecular structure of U–O compounds. Based on the MRS results it was possible to determine the mineral phases of U oxides in the U-rich particles collected in the closed U mine in Hungary. Apart from the forms as  $\text{U}_3\text{O}_8$  and residues of  $\text{UO}_2$ , which are relatively immobile in the environment, the presence of a transportable form as U(VI) was also detected.

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