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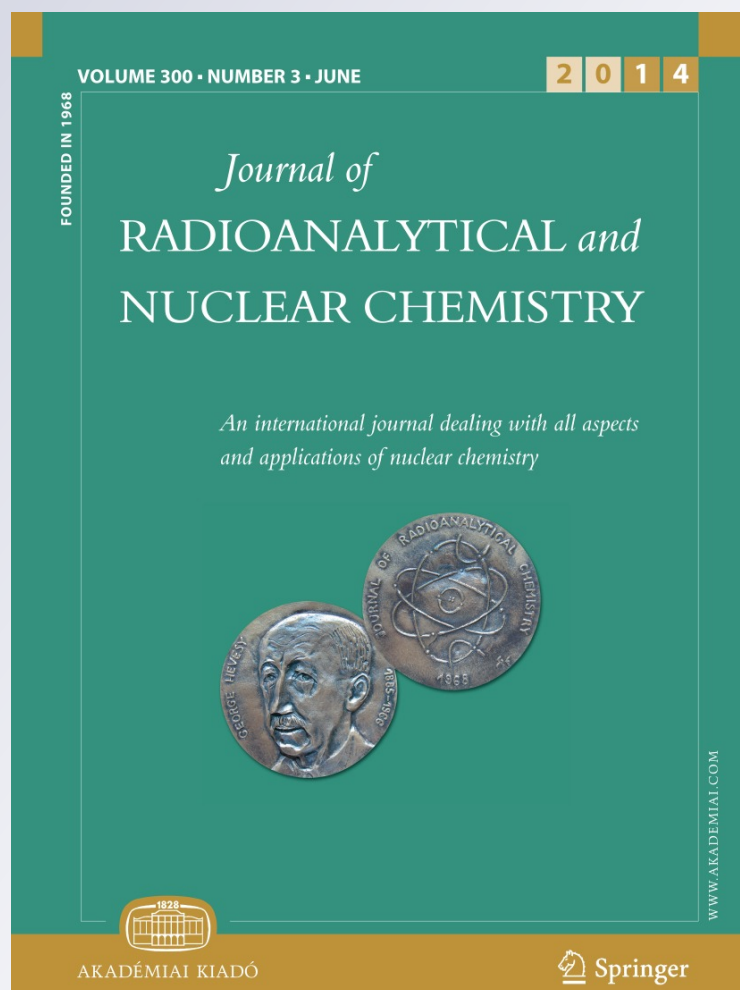
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Preparation of pure TiO₂ sorption material

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Abstract Determination of ²³⁶U/²³⁸U at natural ratios using accelerator mass spectrometry (AMS) requires overall purity of each step in the sample preparation procedures which are complex and include various chemicals. Therefore, the simplification of the procedures is desirable and can be done by implementing other effective separation materials. Among the prospective sorption materials, hydrated titanium dioxides showed promising properties for uranium extraction from various water samples. This paper shows the preparation of several titanium based sorption materials using an organic precursor and their characterization with several techniques in order to analyse crystal structure (XRPD, SEM, HRTEM, SAED) and residues of organic compounds (TG analysis and IR spectroscopy) and to quantify their sorption properties towards uranium. The practical sorption capacity of one of the prepared materials was as high as 260 mg of uranium per gram. AMS measurements showed that it is possible to prepare sufficiently pure titanium dioxides for the determination of ²³⁶U/²³⁸U ratio.

Keywords Titanium dioxide · Uranium · AMS · Sorption

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Introduction

Among environmental sample analyses the determination of ultra-low ²³⁶U concentrations has been recently included [1–3]. In such ultra-trace analyses, the purity of sorption materials is very important and the traditional preparation procedures have to be optimized to minimize possible contamination. In the case of the determination of ²³⁶U/²³⁸U at natural isotopic ratios (²³⁶U/²³⁸U ~ 10⁻¹⁰–10⁻¹⁴), the sample treatment procedure has to be modified in order to eliminate possible contamination from anthropogenic ²³⁶U that may result even in more than a million times higher ²³⁶U/²³⁸U ratios [4]. The main disadvantages of the procedures used for the sample treatment are the complexity and the number of separation steps and chemicals which are not usually monitored for the uranium contamination [5–7].

One of the possibilities to minimize the number of separation steps and to simplify the procedure is the application of effective separation materials. Many inorganic and organic materials have been proposed for the extraction of uranium [8]. However, only several of them are suitable for the uranium sorption from the solutions of low uranium concentration, but relatively high salt content, such as fresh water, sea water etc. At the same time they have to meet other limiting parameters such as fast kinetics, chemical stability, and low costs [9]. Among the inorganic sorption materials, titanium dioxide has been studied for years with promising results [10].

Titanium dioxides can be prepared via the hydrolysis of titanium compounds, either inorganic salts or organic derivatives [11, 12], but their properties strongly depend on the preparation conditions. One of the aspects which should be considered in the preparation of TiO₂-based absorbers is the fact that the sorption properties of titanium dioxides strongly depend on their crystal structure and their capacities increase

in order: rutile<anatase<amorphous [13]. Amorphous oxides have lower long-term stability because they transform into crystalline structure after increasing the temperature or after ageing [14]. The mechanism of radionuclide sorption on titanium dioxide have been published in many studies in addition with the influences of surface area, ionic strength, various anions etc. [15, 16].

In classical procedures, titanium dioxides are prepared from commercial inorganic salts, such as sulphates or chlorides, or even from industrial intermediates of the titanium white production. Typically, the resulting titanium dioxides are contaminated with uranium already from the origin [17]. Assuming that most organic compounds do not contain uranium, titanium dioxide free of uranium contamination could be prepared by the hydrolysis of organic titanium derivatives using “uranium free” water and/or water that has been isolated from the natural water circulation for at least last 100 years (since the beginning of the “nuclear era”), thus not contaminated with anthropogenic uranium.

The aim of this study was to optimize the preparation procedure of titanium dioxide from an organic precursor with respect to the sorption properties towards uranium and in parallel to confirm the purity of the proposed product, resp. the uranium absence in the resulting material, using accelerator mass spectrometry (AMS).

Experimental

Reagents and Chemicals

For the basic chemical studies, most of the materials were prepared from TBOT (tetra-*n*-butylorthotitanate, $C_{16}H_{36}O_4Ti$, Merck). Acetone and ethanol were technical grade, isopropanol, ammonia solution and uranyl nitrate were p. a. commercial preparation.

In the experiments devoted to the preparation of pure titanium dioxide for AMS measurements the same organic precursor was used, but the other chemicals were replaced. The source of “uranium free” water was chosen following several prerequisites, but the main one was its isolation from the natural water circulation for at least last 100 years. Source of such water was found in Decin (CZ) thermal water with an estimated age of 24,800 years [18]. The additional advantages of this water source were the over-pressurization in the underground and relatively low level of mineralization ($\sim 500 \text{ mg L}^{-1}$). In order to minimize the salt content, thermal water was distilled in brand new distillation apparatus.

Titanium dioxide preparation

The conditions of the procedures slightly varied but the important steps like sample drying remained unchanged.

Table 1 List of chemicals used in the preparation of titanium dioxide T1–T5 (IP—*i*-isopropanol, W—distilled water, AC—acetone, AM— NH_4OH , EtOH—ethanol)

	Chemical A	Chemical B	Chemical C
T1	TBOT	IP + AM	AC
T2	TBOT	IP + AM	EtOH
T3	TBOT	W	AC + EtOH + W
T4	IP + W	TBOT	–
T5	W	TBOT	AC + EtOH + W

The preparation procedures of titanium dioxide T1–T5 can be simplified as follows: chemical A is added into the beaker with chemical B while placed in the ultrasonic bath. Then, the material formed is washed with chemical C by decantation. The procedures are clearly described in Table 1.

During the washing steps, the suspension was stirred and then let to settle before removing the liquid over the titanium oxides. The prepared oxides were dried at the maximum of 30 °C in the vacuum dryer not to lose crystal water from the structure ($p \sim 0.5 \text{ kPa}$) [13, 14].

The material T6 was prepared from its water suspension produced as an industrial intermediate from the sulphate process of titanium white production in Precheza, a. s., Prerov, CZ. The suspension was mixed, filtered and washed with distilled water. The oxide was dried in furnace at 45–50 °C [19].

Each material was sieved through USA standard test sieve (Newark) with the mesh size of 125 μm and all experiments were performed with the fraction of grain size $<125 \mu\text{m}$.

The pure hydrous titanium dioxide T7 was prepared using a modification of the procedure for T5 preparation due to its simplicity and usage of only two chemicals in the hydrolysis step itself. Water distilled from Decin thermal water was used instead of lab distilled water and was also used together with acetone for the washing step. T7 material was then used for uranium sorption from crude thermal Decin water. 2 mL column was filled from the bottom with a piece of filter paper Whatman GF/C, a frit and 200.8 mg of T7 material. 1,012 mL of crude Decin water was pumped through the column. At the beginning, the flow rate was 30 mL h^{-1} and it slowly decreased to 15 mL h^{-1} as the pores were blocked with TiO_2 particles. This loaded material was marked as T8. Both T7 and T8 materials were dried using the same conditions as mentioned above.

Instruments

Phase identification of the prepared materials was investigated by X-ray powder diffraction (XRPD) using Ni-filtered $Cu-K_{\alpha 1,2}$ radiation and a modified computer-

controlled HZG-3 goniometer. Specific surface area was determined using selective sorption of nitrogen gas from a catalytically deoxygenated mixture of 5 H₂: 1 N₂ at the temperature of 77 K. The deficiency of nitrogen in the gas due to sorption on the solid sample was determined by a thermal conductivity detector. Specific surface area was then calculated by relating the area of the desorption peak from the sample to that from TiO₂ standard (48.88 m² g⁻¹, measured by BET). Thermal analyses were performed in a Labsys Evo thermoanalyser in a temperature range between 0 and 1,600 °C and by FTIR spectroscopy (Fourier transform infrared spectroscopy) using a Nicolet Impact 400D spectrometer (the range of 400–4,000 cm⁻¹). The samples were measured in transmission mode as KBr discs. The size and shape of the particles were additionally measured using scanning electron microscopy (SEM, JEOL JSM 6510LV), high resolution transmission electron microscopy (HRTEM, JEOL JEM 3010) and selected electron diffraction (SAED).

AMS measurements

For the AMS measurements the dried T7 and T8 materials were pressed into an aluminium sample holder without any further chemical treatment. The setup of AMS (VERA facility, Vienna, Austria) is described in Steier et al. [20].

Uranium sorption

Sorption capacities for uranium were deduced from their sorption isotherms determined with fixed uranium concentration (10 or 20 mmol L⁻¹) and variable values of V/m (10–1,400 mL g⁻¹). The batch experiments were performed using the materials with the grain size less than 125 μm. The samples were contacted for 2 h using a laboratory shaker PTR-30 (Grant-bio, United Kingdom). The suspensions were filtered using glass microfiber filters Whatman GF/C and the uranium concentration in the filtrate was measured using a Liquid Scintillation spectrometer Triathler (Hidex Oy, Finland).

Results and discussion

X-ray diffraction analyses

The phase compositions of all prepared materials are shown in Figs. 1 and 2. These diffraction patterns were compared with the diffraction lines of anatase, rutile, brookite and H_xTiO_y obtained from ICDD-PDF-2 database. T1, T2 and T4 materials showed very broad peaks (Fig. 1) and very low level of crystallinity, and no diffraction peaks

of anatase, rutile or brookite were identified. The peak around 20° (2θ) may correspond to the most intensive line of hydrated titanium oxide H_xTiO_y; however, no other lines were definitely identified. Overall, this means that the T1, T2 and T4 materials are amorphous [13].

On the other hand, the diffraction patterns of T3, T5 and T6 materials (Fig. 2) showed peaks with narrower widths and the presence of anatase and brookite was easily identified. However, the widths of the peaks indicate relatively low degree of crystallinity, showing only a short-range order. This higher level of crystallinity may already imply lower sorption capacities of T3, T5 and T6 materials.

Specific surface

Another material property which influences the capacity of the sorption material is its specific surface area. Table 2 shows the values of specific surface areas of the synthesized materials with the highest value of 307 m² g⁻¹ for T1 material. The results showed the importance of the individual steps in the preparation procedure. The addition of water to TBOT instead of the addition of TBOT to water (Table 1) caused the decrease by 40 % in the size of surface area (T3: 265 m² g⁻¹; T5: 159 m² g⁻¹). Using the same precursor, Crisan et al. [11] prepared titanium dioxide material with the specific surface area of 188 m² g⁻¹ (drying at 80 °C) which fits in the range of values obtained in this study.

No correlation between the size of specific area and the phase composition of the prepared materials was found. Even though T4 material is taken as an amorphous titanium dioxide, the measurements showed very small size of specific surface area (15 m² g⁻¹), even smaller than for T3 and T5 material which showed a certain level of crystallinity.

Differential thermal, gravimetric and IR analyses

The presence of the organic compound residue in the prepared materials after the hydrolysis was monitored using the thermogravimetry and IR analyses. The thermal behaviour of the synthesized materials was studied under static air and inert atmosphere; however, it was found that the change of atmosphere did not cause any significant difference in the shapes of thermogravimetric (TG) and differential thermal curves (DTG). All DTG curves of the titanium dioxide materials showed a broad peak at ~100 °C which can correspond to the removal of absorbed water and butanol (Fig. 3). In addition, the DTG curves of T1 and T2 materials contained a sharp peak at ~250 °C which may be attributed to the degradation of the organic matter (Fig. 3). In the case of calcination at static air

Fig. 1 X-ray diffraction patterns (Cu-K_α) of T1, T2 and T4 materials in comparison with hydrous titanium dioxide H_xTiO_y (ICDD-PDF-2 Database)

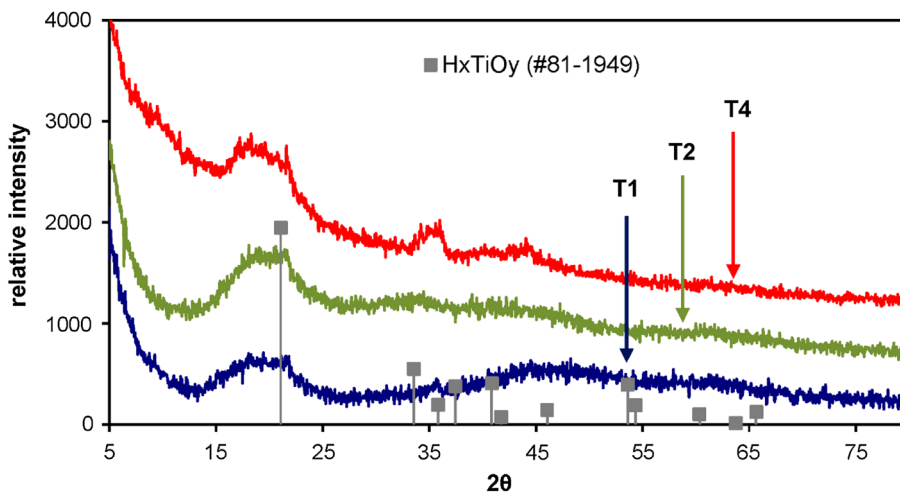


Fig. 2 X-ray diffraction patterns (Cu-K_α) of T3, T5 and T6 in comparison with anatase and brookite (ICDD-PDF-2 Database)

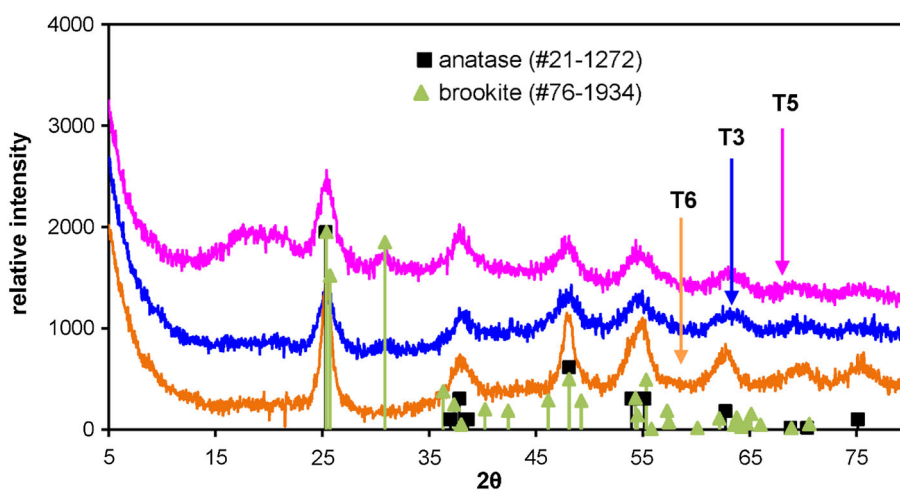


Table 2 Specific surface area (SSA) of synthesized materials

Sorption material	SSA (m ² g ⁻¹)	Sorption material	SSA (m ² g ⁻¹)
T1	307	T4	15
T2	89	T5	159
T3	264	T6	55

atmosphere, this is followed by slow oxidation of carbonaceous residuals demonstrated as a continuous decrease which is not observed in the calcination under inert atmosphere. The absence of the oxidation caused the colour change of the materials from white to black (carbon). This could indicate that T1 and T2 materials are a product of incomplete hydrolyses and that they contain tetra-*n*-butylorthotitanate and/or its hydrolytic products. Consequently, the biggest mass losses were measured for T1 and T2 materials (inert atmosphere: 27 and 29 %, respectively).

IR analysis showed the typical bands of hydrated titanium dioxide in all spectra of the synthesized materials; a wide band

between 500 and 900 cm⁻¹ due to Ti–O stretching vibration and another wide band between 3,000 and 3,500 cm⁻¹ due to Ti–O–H vibration and water in the samples (Fig. 4). The IR spectra of T3, T5, T6 materials confirmed the conclusions from thermogravimetric analyses that these materials contain low or even no amount of organic compounds. In this case, the procedure conditions provided a complete hydrolysis of tetra-*n*-butylorthotitanate; no bands of C–O–Ti vibration at ~1,030 cm⁻¹ were observed in the spectra. On the other hand, the bands attributed to stretching vibrations of aliphatic moieties (2,800–3,000 cm⁻¹) were easily identified in the spectra of T1 and T2 materials. This could be associated with an incomplete hydrolysis of tetra-*n*-butylorthotitanate and with the presence of the compound itself and/or its hydrolytic products as mentioned in the previous paragraph or with the washing step in the preparation procedure. The spectra of T4 material also indicated the presence of organic compound; however, these bands can be attributed also to the butanol which may remain in the sample because the washing step in the preparation procedure of this material was left out.

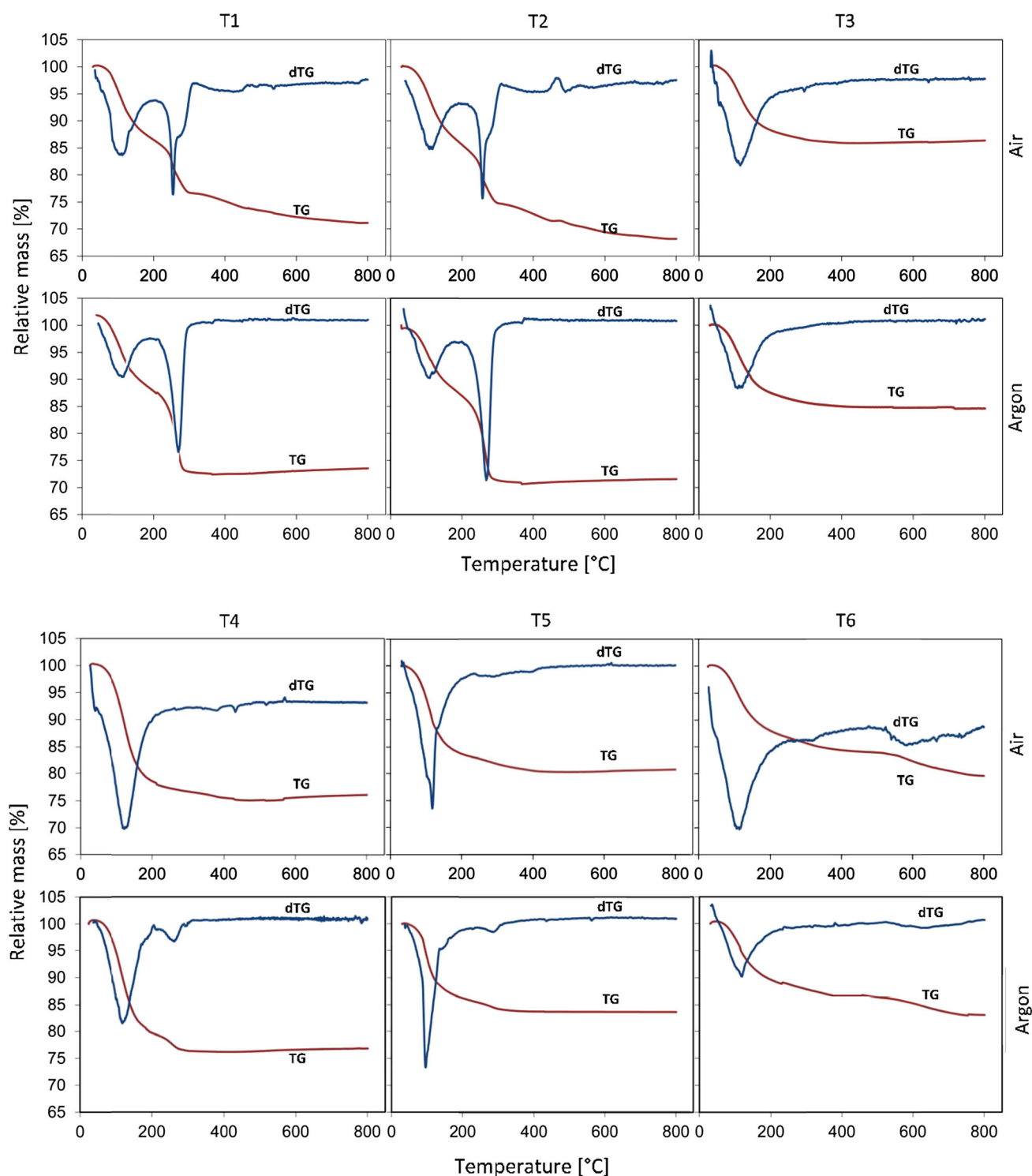
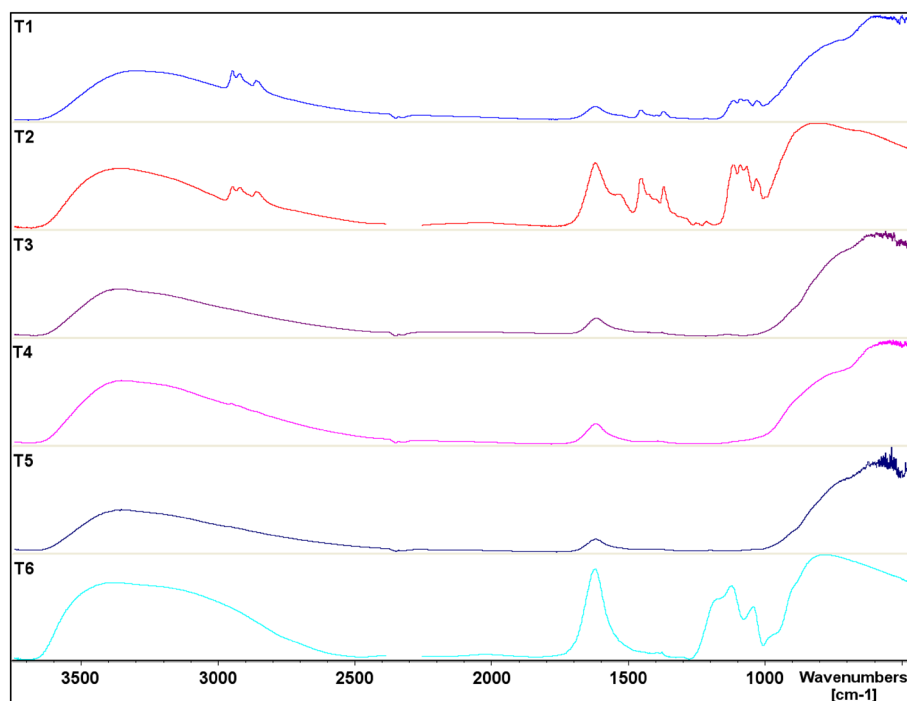


Fig. 3 Thermal behaviour of studied materials under static air atmosphere (up) and inert atmosphere (bottom)

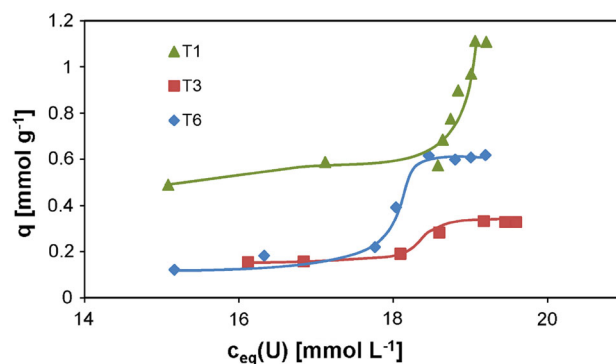
Sorption isotherms

Another important characteristic of new sorption material is a sorption capacity and a possible correlation with specific surface area. In preliminary experiments, the values of

weight sorption capacities q of the synthesized materials ranged between 0.1 and 0.7 mmol g⁻¹ (uranium concentration: 10 mmol L⁻¹, V/m: 50–400 mL g⁻¹) and the limit value of sorption capacity was not reached for any of the studied materials.

Fig. 4 FTIR spectra of studied materials T1–T6

From the above tested materials, three were chosen for more detailed study: T1 due to its high value of preliminarily measured sorption capacity 0.51 mmol g^{-1} ($V/m = 400 \text{ mL g}^{-1}$) and promising properties, T3 as a representative of the materials with higher level of crystallinity (T3, T5 and T6; Fig. 2) and T6 as a reference sample of a hydrolysis product made from inorganic titanium compounds. The detailed sorption isotherm was measured using 20 mmol L^{-1} uranium solution ($V/m: 10\text{--}1,400 \text{ mL g}^{-1}$) and their sorption behaviour can be seen in Fig. 5. As it was expected, the highest q value of 1.1 mmol g^{-1} was measured for the T1 material. It can be seen that the limit value of sorption capacity was still not reached which means that the practical sorption capacity is higher than 260 mg of U per gram of the sorption material. The T6 material showed lower sorption properties towards uranium, approximately 60 % of the T1 sorption capacity, and the T2 material showed even lower one; the results correspond to the conclusions from the diffraction patterns. The shapes of the measured sorption isotherms are not typical indicating that the sorption of uranium on titanium dioxides is complex and based on several sorption mechanisms. The T6 material was used for the TiO-PAN material preparation which was found to be suitable for repeated uranium extraction from aqueous solutions with a practical sorption capacity (10 % breakthrough) of 4.6 mg of uranium per mL of swollen material [21].

**Fig. 5** Sorption isotherms of the T1, T3 and T6 material with eyeguides (initial uranium concentration $c(U) = 20 \text{ mmol L}^{-1}$, $V/m = 50\text{--}400 \text{ mL g}^{-1}$, contact time: 2 h)

SEM and TEM analyses

The particle size and shape of the T1 and T3 materials is shown in Fig. 6. These two materials were chosen as the representative of two groups differing in the diffraction patterns and in the presence of organic compounds. The micrographs confirmed the conclusions from the XRPD analyses that the T1 material is amorphous material, while the T3 material showed a certain level of crystallinity. It can also be seen that the particles in the materials differ in the size and also in the shape.

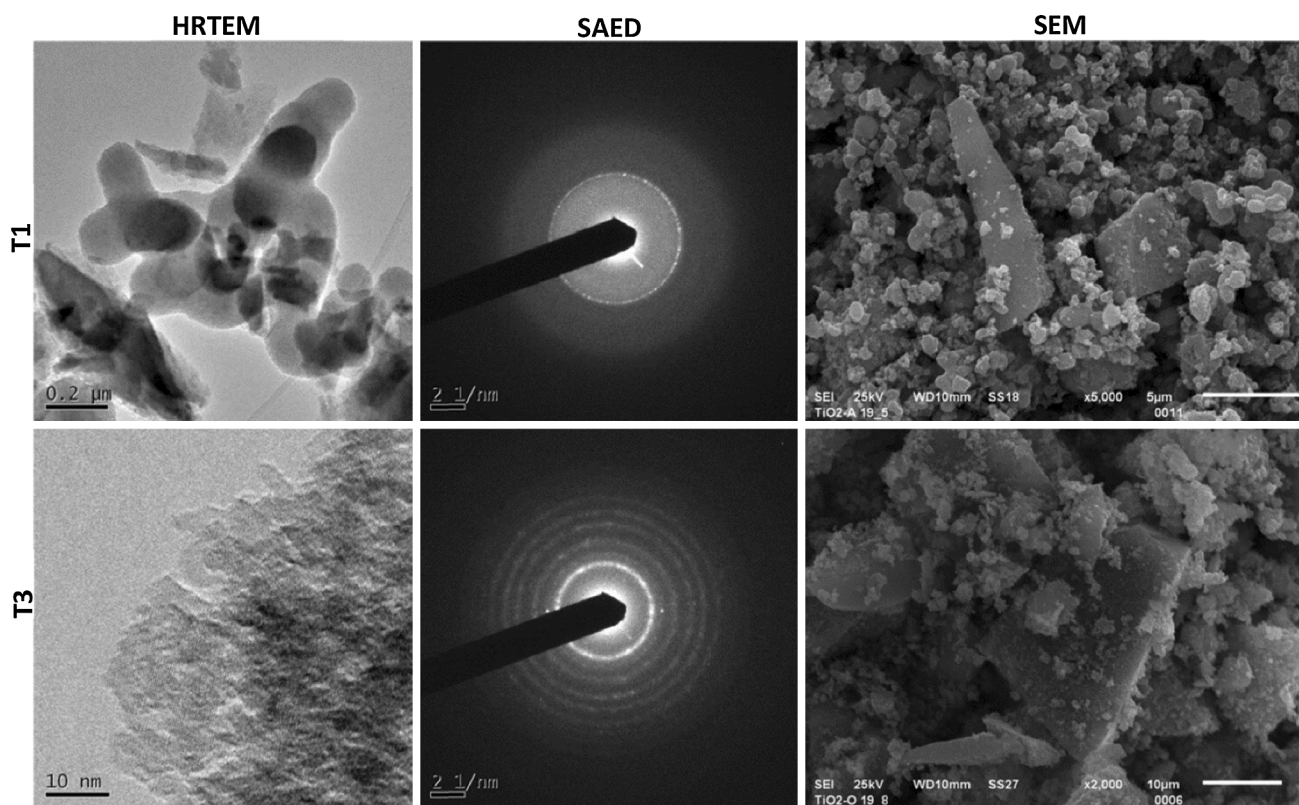


Fig. 6 HRTEM, SAED and SEM images of T1 and T3 materials

AMS measurements

The uranium mass and ^{236}U content were analysed only in the T7 and T8 materials using AMS with direct U^{5+} or U^{3+} ion detection and for some samples TOF analysis. Samples were measured against the Vienna-KkU in-house standard [22]. The results for T7 showed that uranium content in the sample was close to the detection limits and was estimated as 4.5 ± 3.3 ng per sample. ^{236}U with a much lower count rate of 0.330 ± 0.194 s^{-1} was detected which corresponds to a few hundred counts in the typical measurement time. The calculated $^{236}\text{U}/^{238}\text{U}$ ratio $2.04 \times 10^{-5} \pm 3.42 \times 10^{-6}$ is high mainly due to the very low amount of detected ^{238}U . In comparison, in environmental samples the usual ^{238}U mass is around a few micrograms. As for the T8 sample, the uranium content was estimated as 3.1 ± 2.2 ng per sample and the ^{236}U count rate was 0.219 ± 0.212 s^{-1} with $^{236}\text{U}/^{238}\text{U}$ ratio $1.25 \times 10^{-5} \pm 6.35 \times 10^{-6}$. The relative uncertainties come from the repeatability of the measurements. TiO_2 was used as a target matrix for ^{236}U measurements for the first time and thus more experiments have to be carried out to confirm its suitability for this purpose.

Conclusions

Prepared sorption materials (hydrated titanium(4+) oxides) were sufficiently characterised with several techniques. The results showed that the most promising sorption material for uranium separation is T1 material with its amorphousness and high sorption capacity of more than 260 mg of uranium per gram. Its applicability could be extended by improving its mechanical properties, e.g. by incorporating the oxide into a polyacrylonitrile matrix.

It was also proven that using tetra-*n*-butylorthotitanate and “uranium free” water, it is possible to prepare TiO_2 -based sorption materials sufficiently pure for ^{236}U measurements. However, these absorbers have to be studied in more details as AMS target material and also as a part of the method of ^{236}U determination in the environmental samples.

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