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The Role of a Reference Sample in the Study of the Titanium-Containing Silicas by Ultraviolet-Visible Diffuse Reflectance Spectroscopy

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Abstract—On the example of the silica gel with grown titanium oxide structures, in which titanium has two coordination envirornments (anatase, rutile) we showed the effect of the choice of a reference (MgO, SiO_2) on the shape of the ultraviolet-visible diffuse reflectance spectra and the result of their mathematical processing (the Kubelka–Munk function, first derivative).

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As known, the catalytic, sorption and other functional properties of materials are largely determined not only by the composition but also by the structure of the active sites available on the surface. Therefore the choice of ways for the reliable identification of the local structure of surface sites is an important step in creating materials with desired properties.

On the example of titanium-containing silica gels synthesized by the molecular layering it was shown previously that the ultraviolet-visible diffuse reflectance spectroscopy (DRS) is one of the most available and effective methods to assess the structure of functional groups, including titanium and oxygen atoms [1–3]. In [4, 5] several ways were shown to represent the diffuse reflection spectra [as a dependence of the reflection (R_D), Kubelka-Munk function [$F(R_D)$] and the first derivative of the spectrum ($dR_D/d\nu$) on the wave number (ν), as well as the dependence of the transformed Kubelka-Munk function $\{[F(R_D)\cdot E]^{0.5}\}$ on the energy (E)] for the characterization of molecular layering products, which include surface structures with two or more types of coordination environment of titanium with respect to the oxygen. Since the original matrix (silica gel) in the region of registering the DRS spectra [6] also has an absorption band and can affect their shape, it is important in the study of a modified sample to choose a reference to record the spectra for the estimation of characteristics of titanium products.

The purpose of this paper is to analyze the effect of the reference and the mode of mathematical processing of DRS spectra on evaluating the ratio of different types of the titanium oxide polyhedra synthesized on the surface of silica gel by molecular layering.

Figure 1 shows the DRS spectra of the initial and modified silica gel, taken with MgO as a reference. The edge of the absorption band of the initial silica gel is at 33700 cm^{-1} (Table 1). In the spectral range 33000–15000 cm^{-1}, which includes the absorption band edge of the modified samples at the 23600–23850 cm^{-1} (Table 1), the coefficient of diffuse reflection of the original silica gel, obtained with respect to MgO, is almost constant. Therefore, we can assume that selection of a reference (MgO or SiO_2) has no effect on the estimation of the absorption edge position. However, the presence of absorption band of the initial matrix in the region of 33700–45000 cm^{-1} can have an impact on the shape of the spectra at different variant of their mathematical treatment. To determine the effect of the reference the spectra taken with respect to MgO were compared using the plots obtained either relative to the original matrix, or obtained with respect to MgO, and then recalculated using Eq. (1) with respect to the reflection coefficient of the original silica gel (hereinafter: recalculated spectra with respect to the original matrix).

$$R(\mathrm{DTi/MgO/SiO_2}) = \frac{R(\mathrm{DTi/MgO})}{R(\mathrm{DSiO_2})} \times 100\,\% . \qquad (1)$$

Here $R(\mathrm{DTi/MgO/SiO_2})$ is the diffuse reflection coefficient of the titanium silica obtained relative to

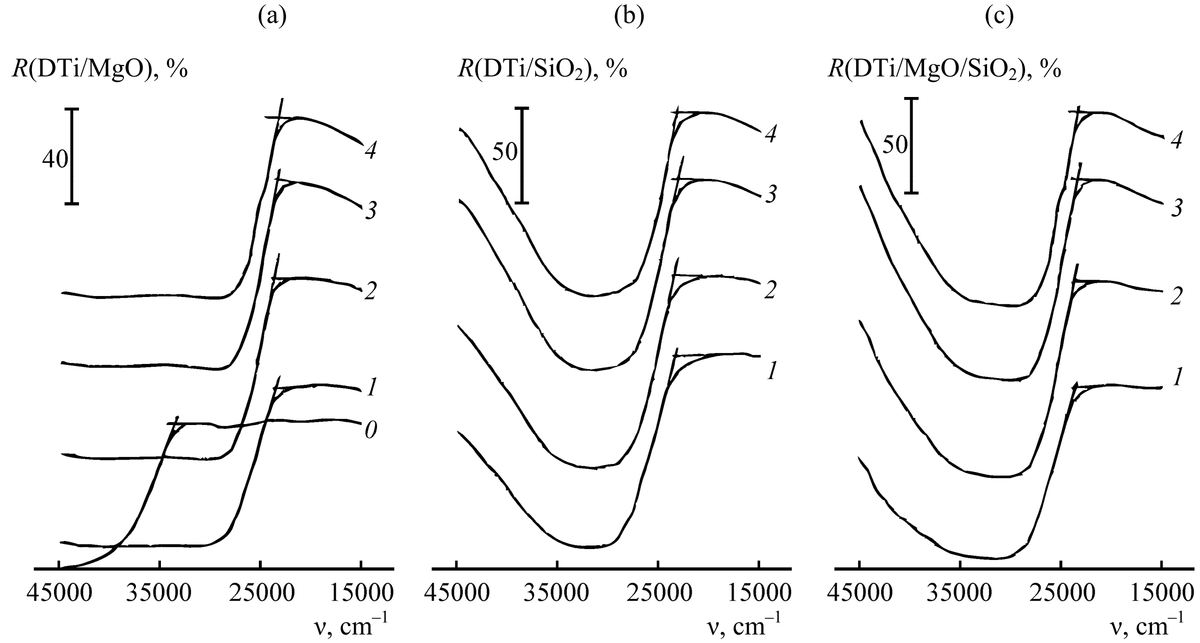

Fig. 1. UV-Vis diffuse reflectance spectra of the original silica gel before (*0*) and after 1 to 4 cycles of synthesis (*1–4*), the reference is (a) MgO, (b) the original silica, (c) and recalculated to the reflectance coefficient of the original silica gel.

MgO and recalculated relative to the coefficient of diffuse reflectance of the initial silica gel, %; *R*(DTi/MgO) is the diffuse reflection coefficient of the titanium-containing silica obtained relative to MgO, %; *R*(DSiO_2) is the diffuse reflection coefficient of the initial silica gel relative to MgO, %.

The recorded spectra (Fig. 1b) and those recalculated with respect to the original matrix (Fig. 1c), are almost identical both by the shape and position of the absorption edge. In both cases there is an increase in the reflection coefficient compared with the spectra obtained with respect to MgO in the region of 15000–30000 cm^{-1}. In the 35000–45000 cm^{-1} (Figs. 1b, 1c), there is an increase in the reflection coefficient due to the presence of absorption of the original matrix (Fig. 1a, the spectrum *0*). Regardless of the use of MgO or SiO_2 as a reference, the positions of the absorption edge in the spectra (Table 1) are similar and are in the region characteristic of the anatase and rutile. Thus, we can assume that the coordination states of titanium atoms in the surface structures and the corresponding crystalline bulk compounds are close.

The absorption edge in the spectrum of the initial silica gel presented as a Kubelka–Munk function $F(R_D)$

Table 1. The positions of the absorption edge in the spectra of anatase, rutile, original and modified silica gel as dependences of R_D on ν

Sample	MgO			SiO_2			MgO/SiO_2		
	nm	cm^{-1}	eV	nm	cm^{-1}	eV	nm	cm^{-1}	eV
Anatase	406	24650	3.06	–	–	–	–	–	–
Rutile	437	22870	2.84	–	–	–	–	–	–
SiO_2	297	33700	4.18	–	–	–	–	–	–
1Ti	424	23600	2.93	426	23500	2.91	424	23600	2.93
2Ti	419	23850	2.96	422	23700	2.94	420	23800	2.95
3Ti	424	23600	2.93	427	23400	2.90	424	23600	2.93
4Ti	424	23600	2.93	426	23500	2.91	426	23450	2.91

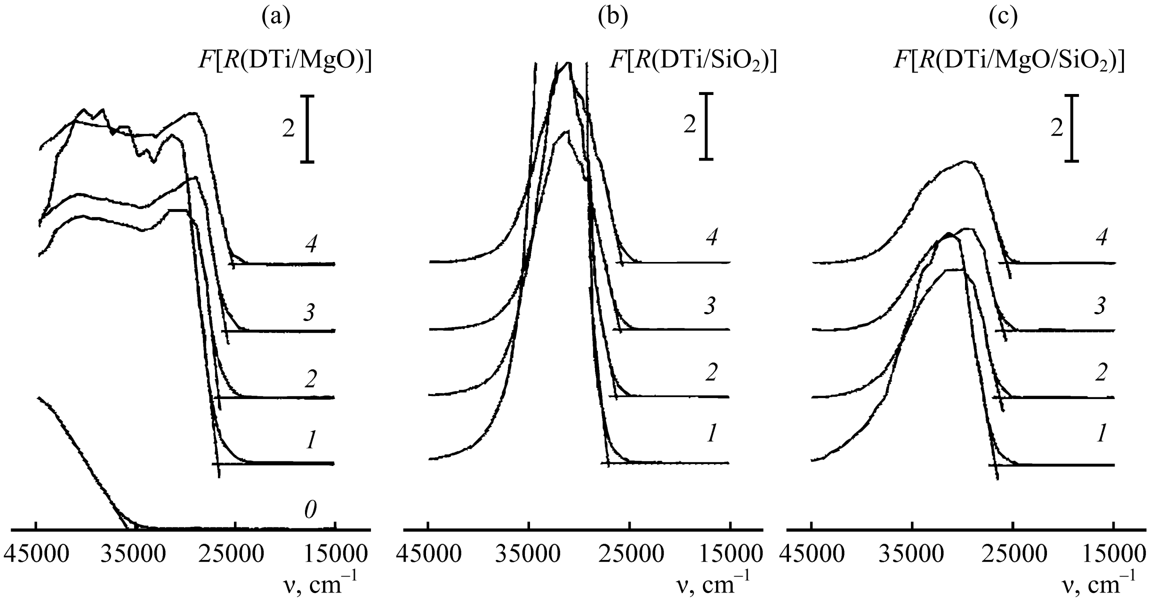

Fig. 2. UV-Vis diffuse reflectance spectra of the original silica gel before (*0*) and after 1 to 4 cycles of synthesis (*1–4*) relatively to MgO (a), original silica gel (b) and expressed as a function $F(R_D)$ (c).

on ν is located at 36 400 cm^{-1} (Fig. 2). A single treatment of silica gel with the $TiCl_4$ and H_2O vapors leads to the formation of a new band. The edge of this absorption band (26 890 cm^{-1}), as well as in the case of R_D–ν spectra, is in the area restricted by the edges of the absorption bands of anatase and rutile (Table 2). It should be noted that while in the case of the R_D–ν spectra the position of absorption edge practically does not depend on the number of treatment cycles, in the case of the representation of the spectrum as a Kubelka–Munk function it is shifted to lower wave numbers. The observed trend may indicate an increase in the proportion of titanium atoms with the rutile-like coordination environment with growing of the titanium oxide structures. Analysis of the series of the directly recorded spectra and those recalculated relatively to the original matrix shows that there is a shift of the absorption edge towards lower wavenumbers with an increase in the number of cycles of synthesis (Table 2). Consequently, just as in the case of processing the R_D–ν spectra, the measured position of the absorption edge does not depend on the choice of the reference against which the spectrum was obtained. The reference change during the spectra recording leads only to a decrease in the value of the function $F(R_D)$ on υ in the range of 35000–45000 cm^{-1} (Figs. 2b and 2c) and may affect the determination of the structure of the titanium oxide structures characterized by the presence of bands in the region of maximum absorption (28000–45000 cm^{-1}).

Figure 3 shows the spectra in the coordinates $[F(R_D)E]^{0.5}$ vs. E. Absorption edge (the width of the optical forbidden gap) for the spectra obtained with different references does not differ significantly (Table 3). The maximum difference 0.05 eV observed for the sample 2Ti can be attributed to the measurement error. The difference module between the values of the absorption edge determined from the $F(R_D)$–ν plot, expressed in eV, and the values of the absorption edge obtained from the $[F(R_D)\cdot E]^{0.5}$–E plot for the corresponding samples did not exceed 0.03 eV. Therefore, the absorption edges determined from the $[F(R_D)\cdot E]^{0.5}$–E and $F(R_D)$–ν plots are almost the same.

The first derivative spectrum of the initial silica gel exhibits a maximum (Figs. 4a and 4b, plot *0*) at 35700 cm^{-1}, which is absent in the derivative spectra of the modified samples, taken with the MgO as a reference.

These results, apparently, are due to a significant absorption in this spectral region by the synthesized titanium oxide structures, which leads to reflection leveling from the original matrix. The same is evidenced by reduced values of the first derivatives of spectra $dR_D/d\nu$ taken with respect to the original matrix in the region of 32000–40000 cm^{-1}.

In the range of 23000–30000 cm^{-1} the first derivatives of the spectra contain two peaks (Figs. 4a and 4b, the plots *1–4* and *1'–4'*) close by the position to the related peaks of anatase and rutile (Table 4). For

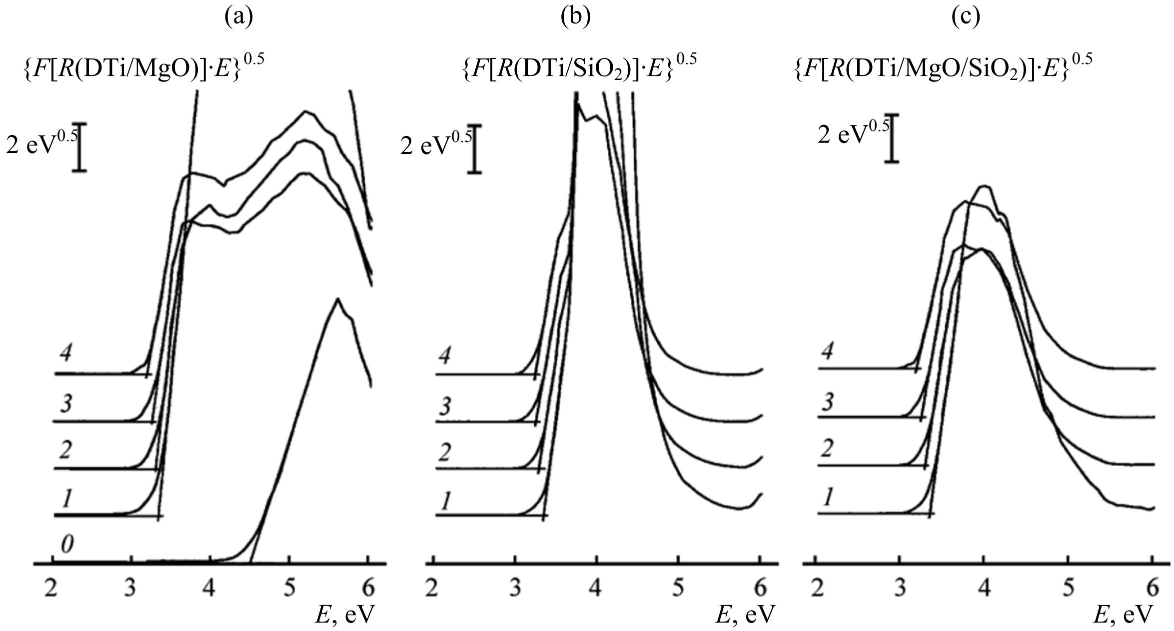

Fig. 3. UV-Vis diffuse reflectance spectra of the original silica gel (*0*) and after 1 to 4 cycles of synthesis (*1–4*) recorded relatively to MgO (a), the original silica (b) and recalculated accounting for the reflection coefficient of the initial silica (c), represented in the $[F(R_D)\cdot E]^{0.5}$–E coordinates.

the sample obtained after single cycle of deposition the intensities of the maxima are practically the same. With the increase in the number of synthesis cycles (increment of titanium content in the samples) there is a tendency to a raise in the intensity ratio of the maximum corresponding to the rutile to that of anatase, regardless of the reference sample (MgO, SiO_2). Hence, with the increase in the number of titanium oxide structures the fraction of the titanium atoms in the coordination environment characteristic of rutile grows.

Thus, it was found that when recording the DRS spectra of the samples of titanium-containing silica gel the choice of a reference compound (MgO or SiO_2) affects the shape of the spectra and their first derivatives in the spectral range 32000–45000 cm^{-1}. However, the position of the absorption edge in the spectra of modified samples is not changed. According to DRS spectra represented as $F(R_D)$–ν, $dR_D/d\nu$–ν and $[F(R_D)\cdot E]^{0.5}$–E plots with the increase of number of synthesis cycles from 1 to 4 a fraction of the rutile-like polyhedra in the deposited titanium oxide structures is growing.

EXPERIMENTAL

Synthesis of the titanium oxide structures on the surface of finely porous silica gel was performed by

Table 2. The positions of the absorption edge in the spectra of anatase, rutile, original and modified silica gel, determined from the dependence $F(R_D)$–ν

Sample	MgO			SiO_2			MgO/SiO_2		
	nm	cm^{-1}	eV	nm	cm^{-1}	eV	nm	cm^{-1}	eV
Anatase	365	27400	3.40	–	–	–	–	–	–
Rutile	418	23900	2.96	–	–	–	–	–	–
SiO_2	275	36400	4.51	–	–	–	–	–	–
1Ti	372	26900	3.34	369	27100	3.36	372	26850	3.33
2Ti	374	26750	3.32	380	26350	3.27	379	26350	3.27
3Ti	383	26100	3.24	384	26050	3.23	383	26100	3.24
4Ti	392	25500	3.16	387	25850	3.20	388	25800	3.20

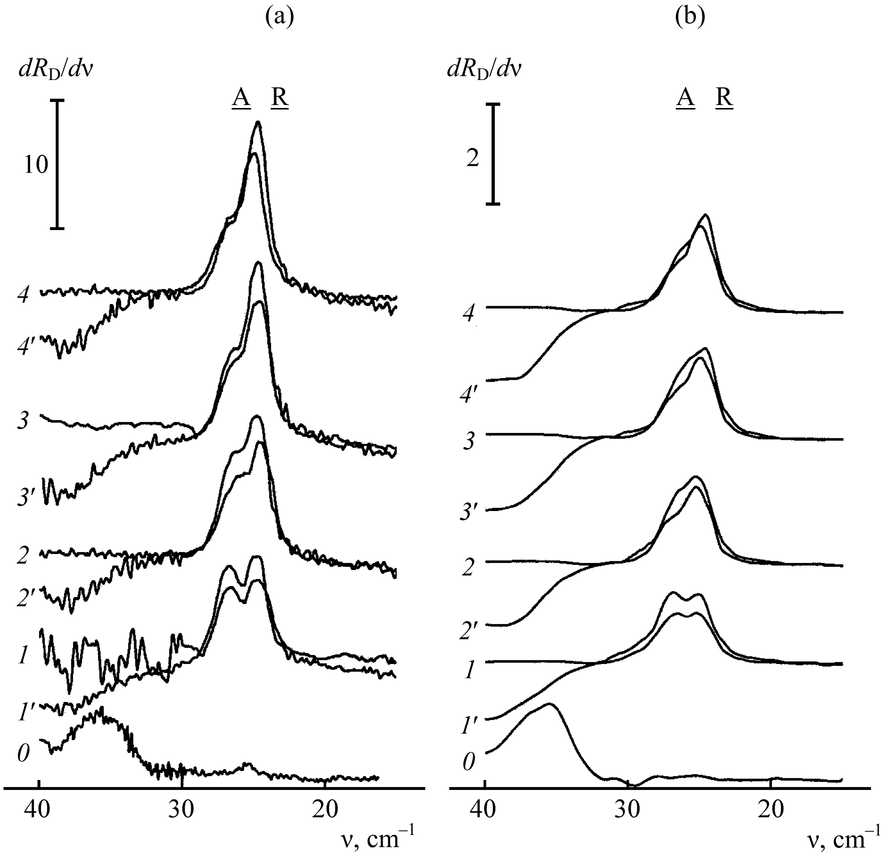

Fig. 4. The first derivative of the DRS spectra of the initial (*0*) and the modified (*1–4*) silica gel after 1 to 4 cycles of synthesis, taken with respect to MgO (*0, 1–4*) and the initial silica gel (*1'–4'*) using hardware (a) and numerical differentiation (b); A, R are the position of the maxima of anatase and rutile, respectively.

the sequential processing the surface with the $TiCl_4$ and H_2O vapors.Therewith, at the surface titanium oxide coordination polyhedra formed characteristic of rutile and anatase modifications [7].

As the silica substrate we used the a finely porous silica from Acros Organics, the product code 240380050, $S_{\text{spec}} = 470$ m^2 g^{-1}, $d_{\text{pores}} = 6$ nm, $V_{\text{pores}} = 0.67$ cm^3 g^{-1}. The synthesis of the titanium oxide structures by a sequential treatment with the vapors of $TiCl_4$ (extra pure, TU 6-09-2118-77) and H_2O (GOST 6709-72) was performed at a temperature of 350°C in a reactor with a partition [8]. The number of cycles of synthesis (n_{Ti}) ranged from 1 to 4. As the carrier gas

Table 3. The positions of the absorption edge in the spectra of anatase, rutile, original and modified silica gel, determined from the dependence $[F(R_D)\cdot E]^{0.5}$–E

Sample	MgO			SiO_2			MgO/SiO_2		
	nm	cm^{-1}	eV	nm	cm^{-1}	eV	nm	cm^{-1}	eV
Anatase	374	26729	3.39	–	–	–	–	–	–
Rutile	426	23470	2.91	–	–	–	–	–	–
SiO_2	276	36300	4.50	–	–	–	–	–	–
1Ti	371	26950	3.34	371	26950	3.34	370	27000	3.35
2Ti	376	26600	3.30	379	26400	3.27	376	26600	3.30
3Ti	381	26200	3.25	383	26100	3.24	382	26200	3.25
4Ti	389	25700	3.19	385	26000	3.22	390	25650	3.18

Table 4. Positions and intensity ratio (J_A/J_R) of the maxima of first derivatives of the spectra of modified samples, calculated in different ways

Sample	Specord M40				Spectra 1.9					
	MgO		SiO_2		MgO		SiO_2		MgO/SiO_2	
	cm^{-1}	J_A/J_R	cm^{-1}	J_A/J_R	cm^{-1}	J_A/J_R	cm^{-1}	J_A/J_R	cm^{-1}	J_A/J_R
Anatase	26400	0.53	–	–	26900	0.49	–	–	–	–
Rutile	24100	0	–	–	23980	0	–	–	–	–
1Ti	26700	0.90	26800	0.92	26700	1.00	26900	1.04	26800	1.03
	24900		24900		25300		25200		25300	
2Ti	26200	0.70	26500	0.74	27100	0.60	26600	0.85	27200	0.60
	24700		24900		25400		25400		25400	
3Ti	26400	0.59	26400	0.52	26600	0.65	26100	0.84	26800	0.57
	24800		24800		25100		24700		25100	
4Ti	26600	0.50	26700	0.45	26400	0.60	26300	0.65	26400	0.56
	25100		24900		25100		24800		24900	

was used the nitrogen with the moisture content no more than 16 mg m^{-3}.

UV-Vis diffuse reflectance spectra were recorded on a Specord M40 spectrophotometer equipped with an integrating sphere, in the spectral range 200–600 nm (45000–15000 cm^{-1}). As a reference the samples of MgO and the initial silica gel pre-heated at 350°C were used. The recalculation of the reflection coefficient of modified samples with respect to the original matrix was performed according to Eq. (1).

The polyhedron type was estimated from the positions of the edge of absorption band [9] and the maximum of first derivative of the spectra [7]. Absorption edge was determined by the method of tangents [9] from the $R_D(\nu)$ spectra directly, the spectra presented in the form of Kubelka–Munk function $F(R_D)$ [4, 5] and the function $[F(R_D)\cdot E]^{0.5}$ [10]. The calculation of the Kubelka–Munk function $F(R_D)$ was performed according to Eq. (2) [11]:

$$F(R_D) = \frac{(1 - R_D)^2}{2R_D}, \tag{2}$$

where R_D is the reflection coefficient expressed as a fraction of a unit.

The energy E was calculated by Eq. (3):

$$E = hc\nu, \tag{3}$$

where h is Planck's constant, eV s; c is the velocity of light, cm s^{-1}; ν is wave number, cm^{-1}.

The first derivatives of the spectra were obtained both by hardware differentiation directly in the course of recording (in the Table 4 indicated a Specord M40), and by numerical differentiation of the spectrum using the SPECTRA ver. 1.9 software (in Table 4 designated as Spectra 1.9), followed by smoothing the curve by using the Savitzky–Golay algorithm.

As the titanium dioxide references were used anatase (A-1 Khimprom) and rutile (high purity, TU 6-09-01-640-84).

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