Austrian Journal of Technical
and Natural Sciences, 2026 No 5–6
ISSN 2310-5607

PREMIER Publishing
ppublishing.org

DOI:10.29013/AJT-26-5.6-24-30

A HYBRID SORPTION-SPECTROSCOPIC APPROACH FOR TITANIUM(IV) DETERMINATION BASED ON CONGO RED IMMOBILIZED ONTO SILK FIBROIN

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Cite: *Gofurov A.A., Smanova Z.A., Shahidova D.N., Usmanova H.U. (2026). A Hybrid Sorption-Spectroscopic Approach for Titanium(IV) Determination Based on Congo Red Immobilized onto Silk Fibroin. Austrian Journal of Technical and Natural Sciences 2026, No 5–6.* https://doi.org/10.29013/AJT-26-5.6-24-30

Abstract

A new hybrid sorption-spectroscopic method for the determination of trace amounts of titanium(IV) ions has been developed. The method is based on the immobilization of an organic reagent, Congo Red (CR), onto a natural polymer matrix – silk fibroin (SF). The complexation conditions of Ti(IV) with various organic azo- and hydroxyl-containing reagents were screened in different buffer systems within a pH range of 2.6 to 7.1. It was established that Congo Red selectively forms a stable dark-blue complex with Ti(IV) in an acetate buffer solution at an optimum pH of 4.6, shifting the absorption maximum from 500 nm (reagent) to 575 nm (complex). Among the evaluated sorbents (PPA, PPD, PPM, and silk fibroin), silk fibroin demonstrated superior sorption capacity toward Congo Red. The immobilized matrix changes color upon contact with Ti(IV) ions, showing a diffuse reflectance maximum at λ = 585 nm. The linear range of the analytical signal obeying the Beer-Lambert law is 8–48 μg/L of Ti(IV). The accuracy of the method was validated using artificial solutions, yielding a relative standard deviation (Sr) of less than 0.022. The structural and elemental fixation of the reagent and subsequent sorption of titanium onto the matrix were confirmed by X-ray fluorescence (XRF) analysis, indicating a titanium mass fraction of 2.49% in the target complex.

Keywords: *Titanium(IV), Congo Red, Silk fibroin, Sorption-spectroscopic method, Immobilization, Solid-phase spectrophotometry, X-ray fluorescence analysis*

Introduction

Titanium and its compounds play a pivotal role in modern industrial sectors, ranging from metallurgy and chemical manufacturing to the production of pigments, cosmetics, and advanced biomaterials. However, the inevitable expansion of industrial activities contributes to the progressive accumulation

of titanium(IV) ions in environmental matrices and natural aquatic systems. Although titanium species are generally classified as possessing low systemic toxicity compared to heavy metals, persistent exposure to elevated concentrations can trigger cellular oxidative stress and potentially disturb fragile ecological balances (Zhu, 2026). Consequently, developing highly sensitive, rapid, and cost-effective analytical techniques for the determination of trace titanium(IV) amounts remains a crucial task for environmental monitoring and industrial quality control (Madakkaruppan, 2026).

To date, sophisticated instrumental methods such as Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) have served as the standard benchmarks for trace metal analysis (Falila, 2026). Despite providing exceptional sensitivity and low detection limits, these advanced techniques are frequently constrained by high equipment costs, the need for specialized laboratory infrastructure, and complex, time-consuming sample preparation protocols that prevent on-site, real-time measurements (Gomes, 2025). Traditional solution-based spectrophotometry offers a significantly more economical alternative, yet it often fails to deliver adequate sensitivity when isolating sub-microgram quantities of target analytes and remains highly susceptible to spectral interferences caused by co-existing transition metal ions (Miura, 2025).

To address these challenges, hybrid analytical strategies that integrate solid-phase extraction with direct optical detection have gained widespread traction. By immobilizing a selective organic chromogenic reagent onto a solid support, target ions can be preconcentrated from large liquid volumes and directly quantified on the substrate using solid-phase spectrophotometry or diffuse reflectance spectroscopy (Madusmanova, 2020). This integrated methodology drastically amplifies both the analytical signal intensity and the selectivity of the system, effectively neutralizing the background matrix effects of complex environmental samples without requiring tedious extraction steps (Krasnodębska, 2025).

The critical cornerstone in optimizing these hybrid analytical frameworks lies in the deliberate choice of the solid matrix. While synthetic polymeric sorbents have historically dominated this domain due to their uniform structural architectures, the paradigms of green chemistry have shifted focus toward natural biopolymers. Compelling data reveals that natural sorbents are fully comparable, and in many operational scenarios clearly superior, to their synthetic counterparts (Raut, 2024). Possessing high structural biodegradability, low processing costs, and an exceptional density of native functional groups – such as amino, hydroxyl, and carboxyl units – natural matrices facilitate the stable, spontaneous immobilization of organic ligands through non-covalent and electrostatic interactions without relying on toxic cross-linking chemical agents (Kuminova, 2023).

Among these sustainable candidates, silk fibroin emerges as an exceptionally viable protein matrix for advanced optical test systems due to its robust mechanical strength, high transparency, and chemical resilience (He, 2023). Its porous structure ensures accelerated mass transfer and rapid target ion diffusion during sorption. This research aims to establish a highly selective and sensitive hybrid sorption-spectroscopic method for tracking trace titanium(IV) levels using Congo Red immobilized onto natural silk fibroin (de Higuera, 2022). We outline the optimization of complexation kinetics, compare the system against common synthetic sorbents, and validate it using diffuse reflectance spectroscopy and X-ray fluorescence analysis (Jayawardene, 2021).

Research method

In our study, the research process was divided into several key stages:

1. **Investigation of organic reagents and medium optimization.** The possibility of complex formation between titanium(IV) ions and six organic reagents (magneson-I, Congo Red, Arsenazo III, tropaeolin O, aluminon, and naringin) was evaluated across a wide pH range (2.6–7.1) using glycine, acetate, and ammonium acetate buffer solutions. At the conclusion of this stage, the most suitable reagent was selected.

2. **Spectrophotometric studies in solution.** The absorption spectra of the initial reagents and their corresponding

complexes with Ti(IV) were recorded; the maximum light absorption wavelengths (λmax) and the optimum pH values were determined.

3. **Selection of the polymer matrix.** The sorption capacity of various carriers – specifically the synthetic sorbents PPA, PPD, and PPM, as well as the natural biopolymer silk fibroin – was investigated with respect to the selected organic reagent.

4. **Sorption and structural studies of the modified sorbent.** The spectral characteristics of the immobilized test system were evaluated, the diffuse reflectance spectra of the complex on the matrix were investigated, and the linearity limits obeying the fundamental law of light absorption (the Bouguer–Lambert–Beer law) were established.

5. **Method validation and characterization.** The analysis of model (artificial) solutions was performed along with the evaluation of metrological parameters (S, Sr). Additionally, direct confirmation of elemental fixation was achieved using X-ray fluorescence (XRF) analysis.

Results

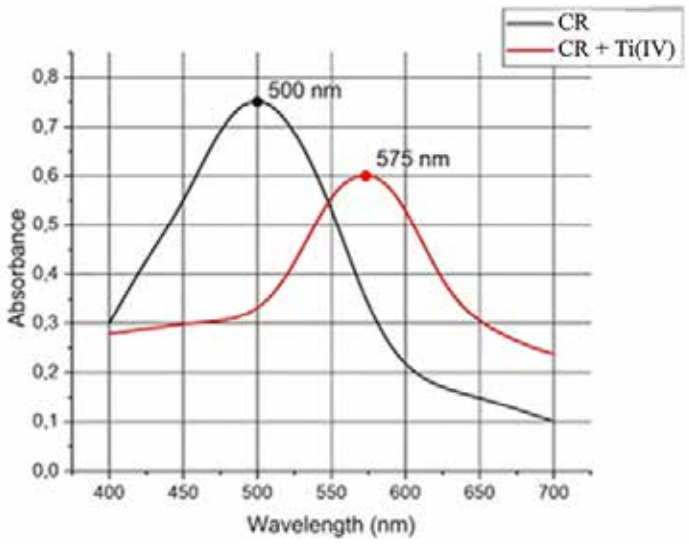
Given that the analytical signal in this study was planned to be acquired spectrophotometrically – by measuring absorbance for solution-based analysis and reflectance for solid-phase (sorbent) analysis – we investigated the feasibility of complex formation between various reagents and titanium(IV) ions across different media and pH levels (Table 1).

Table 1. *Evaluated organic reagents, buffer systems, and pH values examined for complex formation with titanium(IV) ions*

	Glycine buffer			Acetate buffer				Ammonium acetate buffer		
pH	**2.6**	**3.0**	**3.6**	**4.2**	**4.6**	**5.2**	**5.6**	**6.2**	**6.7**	**7.1**
Magneson I	–	–	–	–	–	–	–	–	–	–
Congo Red	–	–	–	+	+	+	–	–	–	–
Ars III	–	–	–	–	–	–	–	–	–	–
Tropeolin O	–	–	–	–	–	–	–	–	–	–
Aluminon	–	–	–	–	–	–	–	–	–	–
Naringin	–	–	–	–	–	–	–	–	–	–

Note: *"–" – complex not detected / analytical signal absent; "+" – complex formation detected*

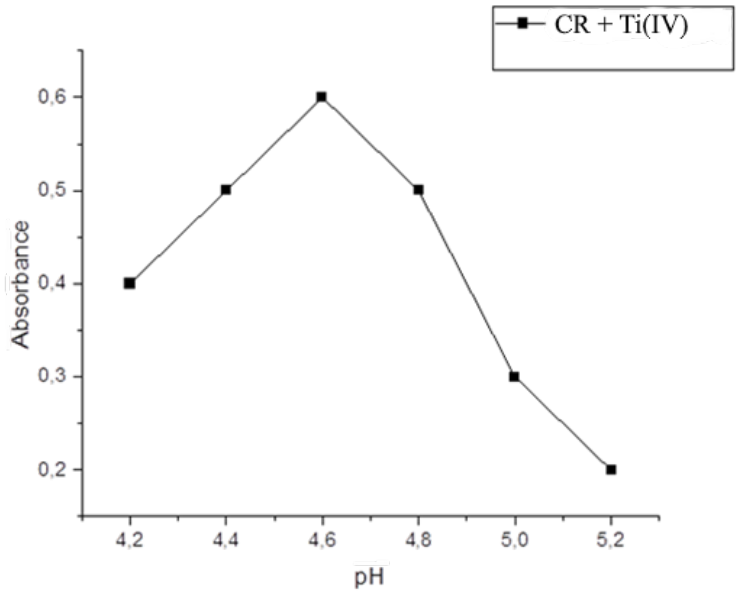
Figure 1. *Light absorption spectra of the Congo Red reagent and its complex with titanium(IV) ions at pH = 4.6 (acetate buffer)*



In our work, we tested several organic reagents, such as magneson-I, Congo Red, Arsenazo III, and tropaeolin O, which contain a diazo group that serves as an effective analytical group capable of complexation. Additionally, aluminon and naringin were evaluated, as they contain phenolic –OH groups bound to a benzene ring and also possess strong potential for forming coordination complexes with metal ions.

We succeeded in obtaining a complex through the interaction of the Congo Red reagent with titanium (IV) ions within a pH range of 4.2–5.1 in an acetate buffer medium. This complex exhibited an absorption maximum at λ = 575 nm. Its color also distinctly differed from that of the reagent itself (Congo Red, λ = 500 nm); the complex turned dark blue, in contrast to the bright red color of the initial reagent (Fig. 1).

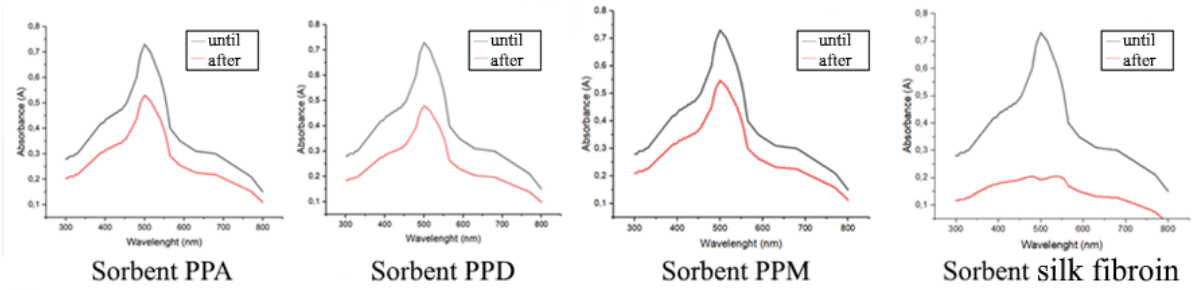
Figure 2. *Light absorption of the complex at λ = 575 nm as a function of the medium pH (acetate buffer)*



It was established that the maximum light absorption of the complex occurs at pH = 4.6. Consequently, all subsequent analyses were performed at this specific pH value to ensure the maximum analytical signal (Fig. 2).

Next, we proceeded with selecting a sorbent for our Congo Red reagent. We investigated its sorption onto various matrices, such as PPA, PPD, PPM, and silk fibroin. Silk fibroin proved to be the most effective sorbent for our reagent (Fig. 3).

Figure 3. *Light absorption spectra of the Congo Red reagent solution before and after immersion of the sorbent for 30 minutes. (C_{CR}= 20 μg/L, $m_{sorb.}$ =0.2 g, V_R=10 mL)*



Upon immersion into a solution containing titanium(IV) ions, the reagent sorbed onto the fiber formed a complex, and the maximum reflectance of the resulting complex was observed at λ = 585 nm (Fig. 4).

Subsequently, the linear range within which the reflectance of the complex –

formed by the interaction of the Congo Red reagent immobilized onto silk fibroin fiber – obeyed the Bouguer–Lambert–Beer law was determined. This linear range was found to be within the titanium(IV) ion concentration spectrum of 8 to 48 μg/L (Fig. 5).

Figure 4. *Dependence of the reflectance coefficient (Kubelka–Munk function) on the wavelength*

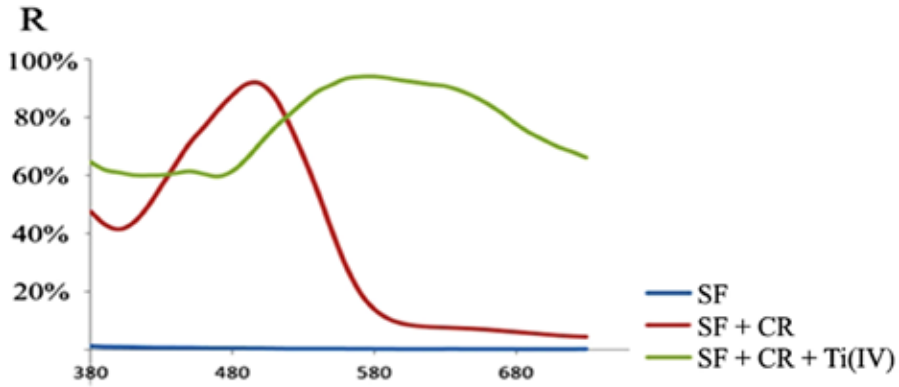
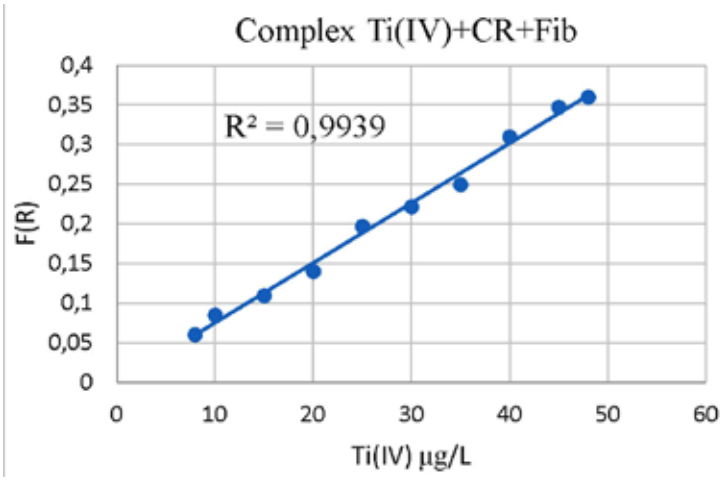


Figure 5. *Linear range of the complex obeying the Bouguer-Lambert-Beer law*



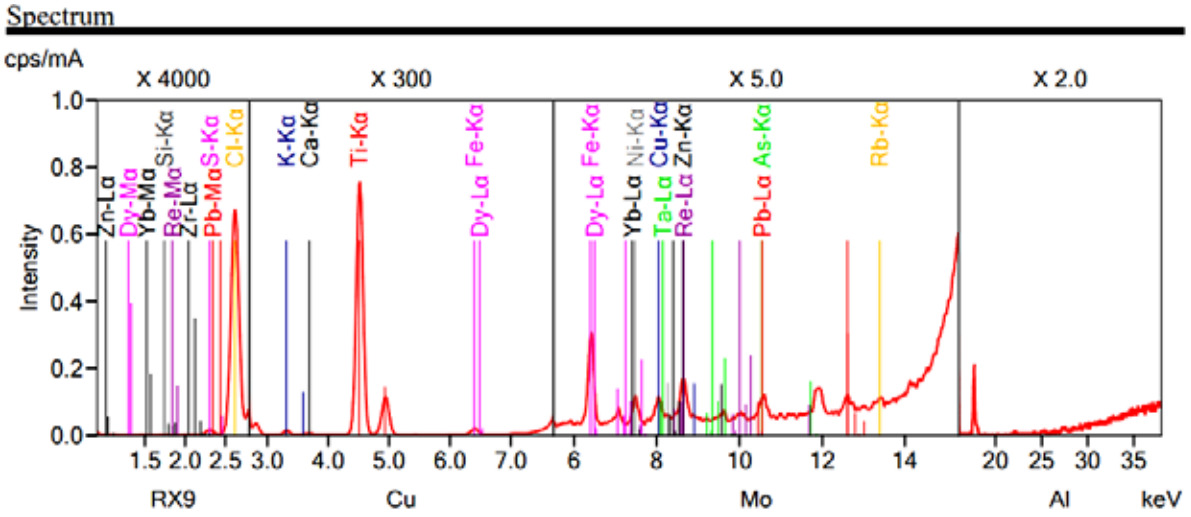
The developed procedure was tested on artificial solutions, which demonstrated its accuracy and feasibility (Table 2).

Table 2. *Analysis of artificial solutions*

Analyzed ion	System	Metal added, μg/L	Metal found, μg/L	S	S_r
Ti(IV)	Fib.: CR	9,0	9,09±0,50	0,200	0,022
		19,0	19,10±0,95	0,382	0,020
		29,0	29,11±1,37	0,553	0,019

X-ray fluorescence (XRF) analysis confirmed the fixation of the reagent onto the silk fibroin fiber, as well as the sorption of titanium(IV) ions onto the modified fiber. The analysis showed that after the interaction of the modified fiber with the solution containing titanium(IV) ions, the mass fraction of the element titanium in the modified fiber was 2.49%, while the mass fraction of the element sulfur, which is part of the reagent, in the fiber was 0.373% (Fig. 6).

Figure 6. *X-ray fluorescence analysis of the complex formed by the interaction of Congo Red immobilized onto silk fibroin with titanium(IV) ions*



Analyzed result(FP method, Scatter)

No.	Component	Result	Unit	Stat. Err.	LLD	LLQ
1	Cl	8.53	mass%	0.0056	0.0027	0.0082
2	Si	0.0966	mass%	0.0026	0.0053	0.0158
3	S	0.373	mass%	0.0022	0.0049	0.0146
4	K	0.184	mass%	0.0031	0.0023	0.0070
5	Ca	0.0423	mass%	0.0013	0.0021	0.0063
6	Ti	2.49	mass%	0.0054	0.0014	0.0042
7	Fe	0.0163	mass%	0.0004	0.0004	0.0012
8	Ni	0.0021	mass%	0.0001	0.0002	0.0006

Conclusion

In the course of the conducted study, a new, highly sensitive, hybrid sorption-spectroscopic method for the determination of micro-amounts of titanium(IV) ions was developed and scientifically substantiated. Based on a comparative analysis of matrices and reagents, the optimal analytical system was selected: the organic reagent Congo Red immobilized on a natural protein carrier – silk fibroin.

The optimum conditions for extraction and the maximum development of a stable optical signal are an acetate buffer solution medium at pH = 4.6 and a working wavelength of 585 nm in the solid phase. The method is characterized by a wide linear determination range (8–48 μg/L), rapid analysis time, high selectivity, and excellent metrological characteristics (Sr≤0.022). The reliability of dye fixation and the occurrence of target component sorption were confirmed by an independent physicochemical method of X-ray fluorescence analysis. The developed hybrid approach can be recommended for the creation of test systems for environmental monitoring and rapid analysis of environmental objects.

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submitted 20.05.2026;
accepted for publication 04.06.2026;
published 30.06.2026

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