

REVIEW

of dissertation for the acquisition of:

educational and scientific degree " doctor "	
scientific degree " Doctor of Science "	X
	the true is indicated by the sign "X"

Author of the dissertation:

Assoc. Professor	PhD	Maria	Atanassova	Petrova	UCTM
academic position	scientific degree	name	middle name	last name	workplace

Topic of the dissertation:

Synergistic solvent extraction of lanthanoids using a combination of chelating and organophosphorus ligands: from ancient beginnings to modern scientific *chefs-d' oeuvre*

Scientific area:

4.	Natural Sciences, Mathematics and Informatics
code	name

Professional area:

4.2.	Chemical Sciences
code	name

Scientific specialty:

Inorganic Chemistry

The review was written by:

Professor	D.Sc.	Vladimir	Bojinov	Bojinov	
academic position	scientific degree	name	middle name	last name	workplace

1. Completion of the provided documents:

A) The dissertation and the competition documents are in full compliance with the Regulations.	4 points	X
B) The documents are complete but do not fully comply with the requirements of the Regulations.	2 points	
C) The documents are not completed in accordance with the requirements of the Regulations.	0 points	
		one of the answers given is marked with the sign "X"

Missing documents and violated standards must be described if response C is marked.

2. Meeting the minimum requirements under the Regulations:

A) The candidate meets the minimum requirements	20 points	X
B) The candidate doesn't meet the minimum requirements	0 points	
		one of the answers given is marked with the sign "X"

It must be filled in if answer B is marked. The publication activity of the candidate is analyzed. The response of the results achieved (quoted) is analyzed.

The dissertation is covered by 18 scientific articles, published in journals with IF, which are cited a total of 232 times in scientific journals, refereed and indexed in the world-leading databases Web of Science and Scopus. With a minimum number of required 100 points, the dissertation collects 410 points only by indicator 7 (Scientific articles published in journals that are refereed and indexed in the world-leading databases Web of Science and Scopus). According to indicator 11 (citation), with a minimum number of 100 points, 464 points are collected. Both indicators have been exceeded more than 4 times!

3. The relevance of the topic of the dissertation:

A) The topic is relevant and new (there are no known results on the topic by other authors)	8 points	
B) The topic is relevant and results from other authors are known	6 points	X
C) The topic is not relevant, but results from other authors are known	2 points	
D) The topic is not relevant and no results from other authors are known	1 point	
E) The topic does not correspond to the level of dissertation	0 points	
		one of the answers given is marked with the sign "X"

The evaluation of the relevance of the dissertation must be substantiated

The growing demand for metals as a major resource for the technological progress of mankind leads to the need to improve and develop the processes of their extraction and purification. Lanthanoids are a strategic class of elements that attract considerable attention due to their exceptional properties related to their magnetic, optical and electronic behavior. They play a significant role in today's high-tech industry and are used in a wide range of environmental technologies, the military industry, energy security and medical diagnostics. In this context, the development of new scientific approaches to the extraction of lanthanoids is and continues to be a hot topic in scientific and industrial circles.

4. Knowledge of the problems, subject of research in the dissertation:

A) The doctoral student knows in detail the achievements of other authors on the topic of the dissertation	8 points	X
B) The doctoral student is partially familiar with the achieved results on the topic of the dissertation	4 points	
C) The doctoral student has no prior knowledge of the status of the problems in the dissertation	0 points	

		one of the answers given is marked with the sign "X"
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The evaluation must be substantiated if answer C is marked.

5. Type of research:

A) Theoretical	4 points	
B) Applied	4 points	
C) Theoretical with application elements	4 points	X
D) It does not correspond to the level of dissertation	0 points	
		one of the answers given is marked with the sign "X"

The level of research must be substantiated if answer D is marked.

6. Objectives of the research:

A) Realistic and of scientific and / or applied interest	8 points	X
B) Realistic, but not of scientific and / or applied interest	3 points	
C) Unattainable (unrealistic)	0 points	
		one of the answers given is marked with the sign "X"

Objectives must be specified. The type of the set objectives must be justified.

The aim of the dissertation is to develop an innovative approach for synergistic extraction of lanthanoids and their separation from organic or ionic liquid media with a combination of chelating and organophosphorus ligands (β -diketones, 4-acylpyrazolones, 4-acylisoxazolones, and calixarenes). The main idea of the dissertation is to examine the role of the chemical structure of the used ligands on the process of 4f-complexation - the influence of cavity size, the size of the macrocyclic structure and its flexibility, hydrophobicity and the presence of different coordinating groups as well as factors governing the stoichiometry of the formed metal complexes and the influence of the solvent on the process of their extraction. The scope of research and the tasks for achieving the set goal are formulated precisely and realistically, and the results achieved based on them are of considerable scientific and applied interest.

7. Methods of research:

A) Adequate to research and set objectives	8 points	X
B) Partially appropriate, enabling part of the scientific objectives and / or applications to be achieved	4 points	
C) Inappropriate methods	0 points	
		one of the answers given is marked with the sign "X"

Methods must be specified. The type of methods used is justified.

To perform the set tasks, protocols have been developed for the conditions of synthesis of chelating and synergistic agents (β -diketones and phosphorus-containing calixarenes) as well as for obtaining their metal complexes in different variations. The obtained products are characterized and proven by elemental analysis, IR and various hydrogen, carbon and phosphorus NMR techniques. Experimental methodologies for the study of the interactions between the extractants and for the conditions of liquid-liquid extraction in a two-phase aqueous-organic medium have been formulated. The distribution (D) of lanthanide ions during synergistic extraction was determined by the slope method, by varying the reagent concentrations, phase volume and pH of the medium. It is worth noting that the used experimental techniques, analytical methods and calculation procedures are a guarantee for high reliability of the results obtained.

The obtained excellent results are in full accordance with the set tasks, which demonstrates a high degree of creative approach in the selection of research methodology to achieve the goals of the dissertation.

8. Contributions of the dissertation:

A) With lasting scientific and / or applied response, they form the basis for new research and applications	20 points	X
B) They are of significant scientific and / or applied interest, complete and / or summarize previous research	16 points	
C) They are of scientific and / or applied interest	12 points	
D) Lack of significant contributions	8 points	
E) Lack of contributions	0 points	
		one of the answers given is marked with the sign "X"

Contributions must be specified. The type of results achieved must be justified.

The dissertation, whose philosophy is based on the creation of a methodology for synergistic extraction of lanthanoid ions, is structured correctly by including all the necessary components, including evidence on the results achieved.

The main contributions of the dissertation could be related to:

- Development of 18 new systems for synergistic extraction of lanthanoid ions in an organic solvent and determination of the process parameters. Various commercial and newly synthesized chelating agents and organophosphorus ligands have been used, mainly calixarenes as synergistic agents, the configuration of which has been determined using a variety of NMR techniques. The mechanisms of extraction and the type of complexes extracted in the organic phase have been established.
- Development of a methodological concept for new techniques of separation and recycling of metals using macrocyclic synergists in the extraction processes. For the first time, the effect of the interaction of a planar molecule with a 3D synergistic ligand is shown, which forms a creative trend for the separation of lanthanoids through the modern design of a new generation of extractants.
- Detailed innovative study with NMR spectroscopy of possible interactions between ligands in the organic phase and their interaction with the organic solvent. No anti-synergistic interaction has been identified.
- Investigation for the first time of synergistic extraction of lanthanoid ions with different combinations of chelating agents and organophosphorus ligands in ionic liquids. The parameters of the process and the factors of influence have been determined, and it has been established that it is possible to be realized more than one extraction model in ionic liquids. Additionally, it has been shown that the synergistic effect is significantly greater in an organic solvent, and for the first time the reasons for reduced synergism in ionic-liquid medium have been formulated.

9. Evaluation of the compliance of the dissertation summary with the dissertation:

A) Full compliance	4 points	X
B) Compliance of the main parts	2 points	
C) Lack of compliance of the main parts	0 points	
		one of the answers given is marked with the sign "X"

The evaluation must be substantiated if answer C is marked.

10. Participation of the doctoral student in the achievement of the results of the dissertation:

A) The doctoral student has at least an equal participation	8 points	X
B) The doctoral student has secondary participation	5 points	
C) The participation of the doctoral student is unnoticeable	0 points	
		one of the answers given is marked with the sign "X"

Critical notes must be provided if one of the items B or C is marked.

Undoubtedly, Assoc. Prof. Atanassova is a leading author in the publications on the topic of the dissertation and is a major contributor to the results achieved. Assoc. Prof. Atanassova is the first author of 16 of the all-18 publications presented. She is the corresponding author of 11 publications, and a sole author of 2 publications.

11. Critical notes:

A) Lack of critical notes	8 points	X
B) Critical notes of a technical nature	7 points	
C) Critical notes that would partially improve the results achieved	4 points	
D) Significant critical notes	0 points	
		one of the answers given is marked with the sign "X"

Critical notes must be provided if one of the answers C or D is marked.

The dissertation is a significant and original contribution to science. Nevertheless, some controversial questions can be addressed to it, the most important of which are:

- First, it is noteworthy that the approach to research largely overlaps with that of the PhD dissertation, where quaternary ammonium salts are used as a synergistic additive. In this connection, the question arises about the effect and advantages of the phosphorus-containing calixarene agents used in the present work, both over the quaternary ammonium salts and over the widely used in practice crown-ethers, from a technological and economic point of view for future industrial applications.

- On page 100 of the dissertation, it is said that the samples are shaken mechanically at 120 rpm for 45 minutes at room temperature, which is sufficient to reach equilibrium. However, it is not clear what exactly is this "shaking" is (obviously it is not stirring) and whether the necessary phase surface is reached under these conditions. Are there any observations on whether and how the shaking rate affects the extraction rate? In addition, does the concentration and volume of the phases affect the process?

12. Conclusion

A) The evaluation of the dissertation is POSITIVE	This evaluation is assigned to a total number of at least 65 points	X (98 points)
B) The evaluation of the dissertation is NEGATIVE	This evaluation is assigned to a total number below 65 points	
		one of the answers given is marked with the sign "X"

To be filled in at the request of the reviewer

The dissertation ***contains scientific and scientific-applied results, which represent an original contribution to the science*** and meet the requirements of the Law for Development of the Academic Staff in the Republic of Bulgaria (LDASRB), the Regulations for application of LDASRB and the Regulations for application of LDASRB of University of Chemical Technology and Metallurgy.

Taking into account the comprehensive and monographic nature of the presented dissertation, its significant fundamental and scientific contributions as well as its remarkable scientific indicators, which drastically exceed the minimum requirements and quantitative criteria, I confidently give a ***positive assessment*** of it and ***recommend on the respected Scientific Jury to confer the scientific degree "Doctor of Sciences"*** on Assoc. Prof. Dr. Eng. Maria Atanassova Petrova in the scientific area 4. Natural Sciences, Mathematics and Informatics, professional area 4.2. Chemical Sciences, scientific specialty "Inorganic Chemistry".

07.06.2022	The review was written by:	
date		signature