

**REVIEW**

of dissertation for the acquisition of:

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

**Author of the dissertation:**

Assoc. Prof.	PhD	Maria	Atanassova	Petrova	University of Chemical Technology and Metallurgy
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:**

Assoc. Prof.	PhD	Kiril	Blazhev	Gavazov	Medical University of Plovdiv
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 based on 18 scientific papers in international journals with IF (WoS), published in the period 2007–2022. The predominant part of them (11) are in journals of the first quartile (Q1). The total number of citations observed in Scopus exceeds 209, which proves the significant scientific response to the results achieved.

## 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 study of coordination and extraction chemistry of lanthanides is relevant due to their unique properties and numerous applications. Separating these elements is a difficult task due to their similar chemical and physical properties. Extraction methods are considered an appropriate solution, but the choice of extractants is of paramount importance to achieve the set objectives. In this regard, the development of new extraction systems for lanthanides is necessary, along with clarifying the chemistry of ongoing processes, especially when using synergistic mixtures containing innovative multicentre ligands, ionic liquids, etc.

It should be noted that the published studies of other authors devoted to liquid-liquid extraction of lanthanides with macromolecules of the calixarene type to create a synergistic effect are sporadic and few. The present dissertation is the first systematic attempt to investigate synergistic solvent

extraction using combinations of calixarene (or smaller phosphorus-containing molecules) and planar-type chelators containing oxygen donor atoms. It fills a gap in the scientific literature and contributes to raising levels of knowledge on specific issues in extraction chemistry, adding three-dimensionality, new ideas and new perspectives.

**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"

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 set objectives are realistic. They are related to the study of the possibilities of synergistic extraction systems for extraction and separation of lanthanides in molecular or ionic liquid media.

Emphasis is placed on the use of phosphorus-containing synergistic agents such as calixarenes. Six objectives and eleven specific questions have been formulated, the answers to which have led to scientific and applied scientific contributions. The objectives include assessment of the influence of the molecular architecture of extractants on the process of complexation and synergistic extraction, optimization of extraction by changing the organic phase (including the use of ionic liquids) or ligand's chemical adjustment, determining the behaviour of the synergistic agent in ionic medium, design of new extraction systems and ultimately achieving efficient and selective extraction.

#### 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.

The methods used are adequate to the set objectives. The slope analysis method has been used to study the extraction. With its help reliable data on the equilibrium constants and stoichiometry of the extracted complexes have been obtained. A set of many spectroscopic, microscopic and thermoanalytical methods has been used to solve the specific scientific problems: UV-Vis, ICP-OES, AAS,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR,  $^{31}\text{P}$  NMR,  $^{19}\text{F}$  NMR, ROESY, NOESY, COSY, HSQC, HMBC, FTIR, ES-MS, X-ray, SEM, TEM, DTA-TG and EPR.

#### 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.

5 main contributions of the dissertation and 22 conclusions have been formulated. The publications on which the mentioned formulations are based have a significant scientific response. I believe that they could serve for a long time as a basis for new research with a scientific and scientific-applied focus.

Contributions:

- A concept has been developed on how macrocyclic 3D molecules can be used as a synergistic agent in extraction processes, leading to new separation techniques and new ways to recycle metals.

- It is shown for the first time how the interaction between a planar molecule and a three-dimensional structure of a synergistic ligand can be used in a self-assembled solvent system for metal ion separation. This leads to new insights into the design of next generation extractants for lanthanoid.
- The potential interactions in the organic phase have been studied in detail (using NMR). It has been found that the increase in synergistic extraction of metal ions depends both on the nature and strength of the possible interactions between the two ligands and on the diluent-ligand interactions.
- Synergistic extraction of lanthanide ions with mixtures containing chelating agents and organophosphorus ligands (e.g., calixarenes in ionic liquids) has been systematically investigated. The parameters of the extraction process have been determined and the synergistic effect and selectivity in the 4f-series have been evaluated.
- It has been found that the synergistic effect in ionic-liquid media is usually much smaller than when using organic solvents. For the first time, an explanation has been proposed for the destruction of synergism in an ionic-liquid medium.

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

A) Full compliance	4 points	
B) Compliance of the main parts	2 points	X
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.

**11. Critical notes:**

A) Lack of critical notes	8 points	
B) Critical notes of a technical nature	7 points	X
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.

## 12. Conclusion

A) The evaluation of the dissertation is <b>POSITIVE</b>	This evaluation is assigned to a total number of at least 65 points	X
B) The evaluation of the dissertation is <b>NEGATIVE</b>	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
Based on the above, I recommend the scientific jury to award the degree of Doctor of Sciences in the professional field of Chemical Sciences (Inorganic Chemistry) to Assoc. Prof. Eng. Maria Atanassova Petrova, PhD.

7.06.2022	The review was written by:	
date		signature