Appendix 12b

REPORT

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. Prof.	**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 science, mathematics and informatics
code	name

Professional area:

4.2.	"Chemical Sciences"
code	name

Scientific specialty:

"Inorganic Chemistry"

The report was written by:

Assoc. Prof.	PhD.	Angelina	Konstantinova	Popova	UCTM
academic position	scientific degree	name	middle name	last name	workplace

1. 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 is mandatory to fill 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 an impressive number of scientific publications in early journals - 18 issues, of which: 11. are for Q1; 6 pcs. for Q2 and one for Q3. These publications carry 410 points, with a minimum requirement of 100 points. In 16 of them the candidate is the first author. She also presented 209 citations, which carry 418 points with a minimum requirement of 100 points. It is obvious that the candidate exceeds the minimum requirements many times over. The abstract fully corresponds to the dissertation.

2. 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	X
B) The topic is relevant and results from other authors are known	6 points	
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
Modern technological progress is associated with the extraction and use of metals. It is important not only the processing of ores, but also the recycling of precious metals from waste in the urban environment, from spent nuclear fuel, from wastewater, in order to reduce environmental pollution and more. The Department of General and Inorganic Chemistry has traditions in the research of liquid-liquid extraction processes and the chemistry of rare earth elements. The development of this topic marks a significant contribution and interest from laboratories from different parts of the world. The industrial use of rare earth elements in the world has increased about 50 times in the last 40 years, which defines them as "critical" metals due to their insufficient availability. Rare earth elements play a significant role in today's high-tech industry - they are used in environmental technology, military industry, energy security and medical diagnostics. These applications are based on various properties derived from their complex electronic structures. The overall demand for technologically important metals is constantly growing. Rare earth elements are also of great importance in nuclear technology. The main method of reprocessing the nuclear fuel used to separate Lns and Ans from the waste stream is liquid-liquid extraction. Synergistic extraction of lanthanides is recommended in the nuclear industry. All this determines the high degree of relevance and significance of the dissertation.

3. Type of research:

A) Theoretical	4 points	
B) Applied	4 points	
C) Theoretical with application elements	4 points	
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.
The research is of scientific and applied nature. The obtained results can find concrete application in practice.

4. Objectives of the research:

A) Realistic and of scientific and / or applied interest	8 points	
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 research is correctly and realistically set and is of scientific and applied science interest. It is to investigate whether a synergistic extraction system comprising a chelated ligand can be used to extract and separate lanthanides in organic or ionic liquid media, using phosphorus-containing synergistic agents, mainly calixarenes. To achieve this, specific tasks have been defined, which have been performed within the framework of extensive and in-depth research.

5. Contributions of the dissertation:

A) With lasting scientific and / or applied response, they form the basis for new research and applications	20 points	
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.
I accept the attached reference for the candidate's contributions. The achieved results can be related to: proving with new means of significant new countries of already existing scientific fields; creating new technologies and obtaining confirmatory facts. The dissertation contains scientific and scientific-applied results, which represent an original contribution to science. I will briefly note the following: 1. Synergistic extraction of lanthanide ions has been studied with 18 new, unexplored systems, including chelating agents and organophosphorus ligands, mainly calixed in their role as synergistic agents in organic solvents. A concept for the use of macrocyclic 3D molecules as a synergistic agent in extraction processes has been developed, leading to new separation techniques and new ways to recycle metals. 2. The mechanism of the extraction process is established. For the first time, it has been shown how to use the interaction between a planar molecule and a three-dimensional (3D) structure of a synergistic ligand in a self-assembled metal ion separation system. 3. For the first time, the potential interactions in the organic phase were studied in detail by NMR spectroscopy. It has been found that the increase in synergistic extraction of metal ions depends on the nature and strength of the possible interaction between the two ligands, as well as on the solvent-ligand interactions: no interaction occurs that causes antisynergism. 4. For the first time, the synergistic extraction of lanthanide ions was studied in detail with ten mixtures, including various chelating agents and organophosphorus ligands, including calixarenes in ionic liquids. The parameters of the extraction process are determined, the synergistic effect is evaluated. It has been found that in some synergistic systems based on ionic liquids, more than one-extraction model can be realized. 5. It has been found that a small synergistic effect, in the range of one to three orders of magnitude, is found in ionic-liquid media, while when organic solvents are used, this increase is much higher - up to 108. For the first time, the cause leading to the destruction of the synergism in the ionic-liquid medium. Given the diligence, organization and very good scientific training of the candidate, I believe that the contributions are largely her work.

6. Conclusion

A) The evaluation of the dissertation is **POSITIVE**	This evaluation is assigned to a total number of at least 40 points	X
B) The evaluation of the dissertation is **NEGATIVE**	This evaluation is assigned to a total number below 40 points	
		one of the answers given is marked with the sign "X"

To be filled in at the request of the member of the scientific jury

Hers presented dissertation is a vast, rich in experimental material, in-depth and competent in its interpretations research. It contains scientific and applied research results that represent a significant and original contribution to science.

The dissertation meets the requirements of the Law for the Development of the Academic Staff in the Republic of Bulgaria (ZRASRB), the Regulations for application of the ZRASRB and the respective Rules of UCTM. The presented materials and dissertation results fully comply with the specific requirements.

Due to the above, I confidently give my positive assessment of the research, presented by dissertation, abstract, results and contributions, and I invite the esteemed scientific jury to award the degree of *"Doctor of Science"* to Assoc. Prof. Dr. Maria Atanasova Petrova in field of higher education 4. Natural science, mathematics and informatics; 4.2. Chemical sciences (Inorganic chemistry).

8.06. 2022	The report was written by: Assoc. Prof. Dr. Angelina Popova	
date		signature