Appendix 12a

REVIEW

of dissertation for the acquisition of:

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

Author of the dissertation:

		Eduard	Lyudmilov	Stefanov	Aurubis AD, Pirdop, Bulgaria
academic position	scientific degree	name	middle name	last name	workplace

Topic of the dissertation:

Speciation Analysis of Arsenic in Copper Electrolytes, Water and Soils.

Scientific area:

4.2	Natural sciences, mathematics and informatics
code	name

Professional area:

4.2	Chemical Sciences
code	name

Scientific specialty:

(Analytical chemistry

The review was written by:

Assoc. prof.	PhD.	Valentina	Veselinova	Lyubomirova	Sofia University, Faculty of Chemistry and Pharmacy, Department of Analytical Chemistry
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.
Eng. Eduard Stefanov has submitted the following documents, according to the requirements for opening a procedure for the defense of a dissertation work of the Regulations for the Acquisition of Scientific Degrees and the Occupancy of Academic Positions of the University of CHEMICAL TECHNOLOGYAND METALLURGY (UCTM): - Application to the Rector of UCTM (according to the template) - CV; - Diploma of completed higher education, Master degree in "Inorganic compounds" at UCTM; - Order №- R-FH 46 from 26.02.2021 for enrollment as a full-time doctoral student at the department: "Analytical Chemistry" in scientific specialty 4.2 Chemical Sciences (Analytical Chemistry); - Protocols for successfully passed exams in the scientific specialty, English language, broad-based and specialized discipline; - Order No. R-FH 27 from 08.02.2024 for deduction with right of defense; - Declaration of authorship; - List of scientific publications included in the dissertation and the full texts of the publications; - Dissertation; - Abstract.

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 results of Eng. Eduard Stefanov are summarized in four scientific publications: two publications in the journal "Archives of Metallurgy and Materials", with IF 0.600; (Q4:12 points), one in Journal of Chemical Technology & Metallurgy, with SJR (10 points), and one without IF and SJR. Part of the results of the dissertation have been reported in three scientific conferences: Poster session for young scientists, doctoral students and students and one international conference: International Conference on Innovative Research (ICIR) Euroinvent in 2021 and 2023. The notices citations on the scientific publications are two.

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
It has long been known that the chemical species of arsenic have different solubility, mobility, bioavailability and resp. toxicity. Inorganic species of arsenic are more toxic than the organic ones, and of these, As(III) is many times more toxic than As(V). The development of methods for identification and quantification of the individual arsenic species is critical to elucidate their distribution, environmental behavior, metabolism, and toxicity. Speciation analysis of arsenic is widely used in environmental monitoring, food control and human health. For this reason, a large number of scientific publications on the speciation analysis of arsenic are known in the world literature, investigating the possibilities of both classical and spectral methods combined with method for separation. In this dissertation, a large number of literary sources are cited, the main part of which are from the last 10-15 years. This shows the continued relevance of the subject. Serious advantages of the dissertation work are: - Development of cheap, fast, accessible methods for analysis with high accuracy and selectivity; - Their application for the determination of arsenic species in copper electrolyte, wastewater and contaminated soils; - Development of an innovative process for wastewater treatment of arsenic by its precipitation as crystalline scorodite ($FeAsO_4.2H_2O$) after oxidation to As(V).

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.
A detailed literature review was made on the subject of the dissertation. A total of 156 literature sources are cited, which demonstrates the in-depth study of the problem and the good ability of the PhD student to use the scientific literature and Bulgarian and European standards.

5. Type of research:

A) Theoretical	4 points	
B) Applied	4 points	X
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.
In the presented dissertation, four methods for speciation analysis of arsenic in samples with different matrix composition were developed. The developed methods will undoubtedly find wide application in analytical practice for the analysis of arsenic species in contaminated samples. Proof of this is the fact that two of the developed methods have already been implemented in the laboratory practice of "Aurubis Bulgaria" AD.

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 present dissertation is to develop cheap, accessible and selective methods for the determination of arsenic species in contaminated samples such as copper electrolyte from the production of cathode copper, wastewater from non-ferrous metallurgy and contaminated soils. The objectives are entirely realistic and include widely used approaches for sample preparation and arsenic determination with accessible analytical methods. The developed methods are optimized at each stage of the analysis and provide serious advantages such as the possibility of complete extraction of the inorganic arsenic species from contaminated soils without changing their chemical form, selective separation and instrumental determination with modern instrumental methods. This determines the high scientific interest: development of a rapid method for sample preparation, use of cheap reagents, high sensitivity, selectivity, reproducibility and accuracy of determination. Undoubtedly, the methods also have a wide applied interest: increasing the quality of produced cathode copper, optimization of wastewater treatment steps by precipitation of arsenic, reduction of wastewater treatment costs.

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 include application of liquid-liquid extraction and ICP-OES/ICP-MS determination of inorganic arsenic species in copper electrolyte, resp. contaminated water and soil. For the determination of the inorganic species in non-ferrous metallurgy contaminated soils, MW dissolution with concentrated hydrochloric acid was applied, prior the separation of the arsenic forms by liquid-liquid extraction and determination by ICP-MS. An innovative and green ion chromatographic method with conductometric detection was also developed for the direct determination of As(V) and total As after oxidation with hydrogen peroxide in a copper electrolyte. The method was also used for the indirect determination of As(III). A statistical evaluation of the methods was also carried out. Mean values, standard deviation, relative standard deviation, standard deviation of mean score, confidence interval, selectivity, presence of gross error was determined using Q-test. The applied set of instrumental methods and statistical evaluation of the methods are fully adequate to the goals and conducted research.

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.
To accomplish the goal of the dissertation, a total of four methods for speciation analysis of arsenic in samples with different matrix composition have been developed as follows: -ICP-OES method in combination with liquid-liquid extraction for simultaneous determination of inorganic species of arsenic in copper electrolyte. -ICP-MS method with liquid-liquid extraction for determination of inorganic species of arsenic in wastewater. -ICP-MS method in combination with MW digestion and liquid-liquid extraction for the determination of inorganic species of arsenic in contaminated soils. - Innovative and green ion chromatography method with conductometric detection for the direct determination of As(V) and total As in copper electrolyte. The method is also suitable for indirect determination of As(III). As the most significant contribution, I would point out the possibility of their real application, the achieved improvement of production processes, the purification of As in wastewater and the prevention of arsenic getting into nature. The developed methods have a lasting scientific and applied impact.

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.
The abstract is presented in 56 pages and is a shortened version of the content of the dissertation. It contains a short introduction, the purpose and tasks of the dissertation work, the research work carried out on optimization of the methods, the obtained results and the statistical evaluation of the methods are well described. The conclusions and contributions of the dissertation research are presented. The abstract adequately reflects the content of the dissertation.

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.
I have no doubt that the presented analyzes and results of the dissertation work of Eng. Eduard Stefanov were obtained as a result of serious theoretical preparation, intensive analytical work and processing of the results. His experience as a PhD student in the Department of Analytical Chemistry of the UCTM and an analytical chemist, quality manager and metrologist at Aurubis Bulgaria AD undoubtedly contributed to the correct performance of the assigned tasks. Proof of the equal participation of the PhD student is the fact that in three out of four scientific publications he is the first author. The stated facts give me reason to believe that the PhD student actively participated both in the implementation of the experimental work, as well as in the processing of the results, the preparation of scientific publications and participation in scientific forums.

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.
I have critical notes of a technical nature on the dissertation work, which do not diminish the value of the dissertation:

1. In the presented list of scientific publications, a technical error was made, as for the journal "Archives of Metallurgy and Materials", Q3 was indicated instead of Q4, but the points were correctly reflected. 2. There are technical errors in the dissertation. For example, in Table 1, containing literature data, errors were made in the indicated concentrations for the content of chemical elements in untreated waste water; when indicating the units of measurement, a dot (µg.L −1) is used; in some places the word order is not properly structured. 3. There are many repetitions in the thesis. I recommend merging a section "Materials and methods" at the beginning of the experimental part. 4. Standard deviations are not presented for some of the analytical results, e.g., in Tables 14, 15, 18, 30, 31, 35. For what reason? 5. Figure 46 presents chromatograms of four standard solutions with the same concentration of F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-} and increasing concentration of As(V) to identify the corresponding retention times. It is noticeable that the NO_3^- peak is absent, and that along with the increase in the area of the As(V) peak, the Cl^- peak also increases. How could this result be explained? 6. A chromatogram from the analysis of As(V) in copper electrolyte samples is not presented in the dissertation, which is of interest and would give the dissertation a more complete look.

12. Conclusion

A) The evaluation of the dissertation is **POSITIVE**	This evaluation is assigned to a total number of at least 65 points	X
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 of Eng. Eduard Stefanov, submitted to me for review contains experimental work with achieved significant results in the field of Analytical chemistry. Four methods were developed for the speciation of inorganic species of arsenic using liquid-liquid extraction and ICP-OES/ICP-MS, as well as an ion chromatographic method for the determination of As(V) and total As. The relevance of the topic, the well-presented information, the presentation of the results in four scientific publications and three participations in scientific conferences fully meet the requirements for the formation of a dissertation work and the Regulations for the acquisition of scientific degrees and the acquisition of academic degrees of UCTM for the acquisition of a scientific and educational degree "Doctor". The total number of points according to indicators from 1-11 is 97. All this gives me reason to POSITIVELY evaluate the doctoral dissertation of Eng. Eduard Stefanov for the awarding of the educational and scientific degree "Doctor" in scientific specialty 4.2 Chemical Sciences (Analytical Chemistry).

30.05.2024	The review was written by:	
date		signature