

**REPORT**

of dissertation for the acquisition of:

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

**Author of the dissertation:**

		Mariya	Tsvetanova	Mondashka	
academic position	scientific degree	name	middle name	last name	workplace

**Topic of the dissertation:**

COMBINED METHODS FOR SEPARATION AND CONCENTRATION OF EXTRACTS FROM NATURAL RAW MATERIALS WITH BIOSOLVENTS
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**Scientific area:**

5	Technical sciences
code	name

**Professional area:**

5.10	Chemical technologies
code	name

**Scientific specialty:**

Processes and apparatus in chemical and biochemical technology
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**The report was written by:**

As. Prof.	PhD	Ilonka	Vasileva	Saykova	UCTM
academic position	scientific degree	name	middle name	last name	workplace

**1. Meeting the minimum requirements under the Regulations:**

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 general impression of the presented dissertation and abstract is the significant volume of precisely conducted experiments and appropriately interpreted results, accompanied by weaker publication activity. It mainly includes participation with posters (4) and reports (3) in scientific forums, one publication in the scientific journal "Scientific Works of UHT - Plovdiv", and only one in which the doctoral candidate is a co-

author, is in a journal with an impact factor (BULG CHEM COMMUN, IF=0.4), with 1 citation in an international publication. The results could be summarized and formatted as a publication in refereed journals.

## 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	
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 dissertation explores a current and significant problem for "green" technologies in the extraction of useful components from plant raw materials, which in the study is focused on the possibilities of limiting or eliminating the use of petroleum-based organic solvents and/or replacing hazardous solvents with safer ones of natural origin. Along with ionic and eutectic solvents, the number of new solvents from renewable sources, in many cases from agrobio waste, the so-called "bio- or agrosolvents", is increasing. The potential for utilizing processed biomass to produce solvents with diverse chemical compositions and a wide range of physicochemical properties is a current field of research. Despite a number of advantages, such as non-toxicity, renewable and biodegradable properties, and environmental friendliness, their wider application in the extraction process is largely hindered by a combination of technical, economic, and regulatory constraints. Furthermore, the use of different solvents for extraction can lead to extracts that differ significantly in the content of various active ingredients, respectively, to different quality and cannot always replace traditional solvents equally.

Given the enormous species diversity of plants, as well as the large number of identified plant-derived compounds, it is important to apply a scientific engineering approach when selecting solvents or extractants for a given application that are theoretically justified from a technical point of view and acceptable from an environmental point of view. In this sense, the issues considered and the solutions presented determine the relevance of the problem developed in the dissertation in two directions - environmental friendliness of the processes and increasing the quality and reliability of plant extracts even in the initial stages of research.

## 3. 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.

The doctoral student's research is aimed at expanding the methodology in the field of solid-liquid extraction using traditional and non-traditional plant-based solvents, with the introduction of environmental indicators and indicators related to the quality and safety of the obtained extracts.

The problem has been approached from two perspectives – from a theoretical-empirical and experimental perspective. The concept of Hansen Solubility Parameters has been applied as an indicative screening tool,

which requires experimental validation of the selected extracting agents. The approach was applied to extract the complex of polar and lipophilic compounds from the medicinal plant St. John's wort (*Hypericum Perforatum*), with the main target components being the herb's characteristic hypericin and its isomers. Based on the formulated criteria for predicting the similarity between the components of the BAV complex and solvents, on the one hand, and compliance with the criteria for environmental friendliness, safety and harmlessness, on the other, over 150 organic solvents commonly used in pharmaceutical chemistry were analyzed (Glaxo Smith Kline's Solvent Sustainability Guide database).

Two-component (water-ethanol and water-glycerol) and multi-component (glyceride vegetable oils) mixed solvents were selected as suitable. Due to the increasing production of biofuels, they are available in large quantities and are one of the cheapest solvents after water. In addition to environmental and economic considerations, they cover a large range of polarity and can be used to directly obtain liquid extracts and extracts enriched with various beneficial ingredients, without additional steps for solvent removal.

To interpret the relationship between the selectivity of solvents (molecular level) and the selectivity of the extraction process (system level) towards the target groups of compounds, the influence of various factors was experimentally studied: extraction method, fractional composition of the raw material, solid/liquid phase ratio, temperature, time and extraction rate.

#### 4. 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.

For the theoretical calculation (prediction) of the solubility parameters, the Hoftyze-Van Krevelen functional group contribution method was used, which allows for sufficiently accurate predictions of the cohesive energy of intermolecular interaction and is easily applicable without the need for specialized software.

For the successful implementation of the concept of environmentally friendly processes and solvents, a comprehensive study was conducted, including characterization of the herb, establishment of appropriate extraction regimes, and verification of the stability and safety with a view to the applicability of the obtained extracts.

To obtain general and partially purified extracts, traditional and non-traditional methods (ultrasound-assisted extraction) were used, which are technologically easy to implement, which is important for successful practical applicability. As quantitative indicators of the quality of the extracts, the content of active substances-markers for the herb (hypericins and flavonoids), determined by established and validated spectrophotometric methods, was used. Based on the experiments conducted, a scheme for the complex use of the raw material and the step-by-step preparation of three types of extracts with different properties and purposes was proposed, which shows the completeness of the scientific idea.

#### 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	x
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"
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Contributions must be specified. The type of results achieved must be justified.

In the conclusion of the dissertation, specific conclusions (6 in number) are made, which reveal various aspects of the research and show the achievements as a result of the conducted research. 2 summarized contributions with a scientific and applied focus and 3 with a practical focus, related to obtaining new data when examining the specific herb, are made. The problem of natural variability in the content and relative share of more important groups of components in the herb depending on the plant parts used (ontogenetic changes) and at different periods of flowering (morphogenetic changes) for six different starting materials is shown, and the need for control and management of the extraction process to ensure a reproducible composition of the extracts. Through experimental determination and modeling of extraction kinetics, the impact of ultrasonic treatment alone and when combined with mechanical agitation and heating to improve mass transfer, especially in vegetable oils, has been confirmed.

There are contributions of a scientific-applied nature, and I would highlight the critical analysis of the applicability and limitations of the Hansen model in predicting which type of solvent may be suitable for a specific process. The results of the comparison of theoretical and experimental data on the dissolving and extracting ability of water-alcohol mixtures and vegetable oils are of significant weight to the contributions of this dissertation work. Such are, for example, the theoretical assessment of solubility parameters taking into account the natural variability of the fatty acid composition of vegetable oils and the use for the first time of some non-traditional oils in the preparation of oil extracts from the herb.

Although the study is based on the already established concept of Hansen solubility parameters, combining them with indicators of environmental friendliness, health safety and occupational safety, before or in parallel with experimental validation, makes it possible to expand the assessment by taking into account other important properties of solvents, and based on the results, to make generalizations about their functional suitability and appropriateness for use in a given application. The approach could be modernized by using more accurate thermodynamic models embedded in modern chemical process simulators (Aspen, ChemCAD, HYSYS) and specialized software products (COSMO-RS), based on quantum-chemical calculations and statistical thermodynamics for solving scientific problems of an interdisciplinary nature and significant practical application.

## 6. Conclusion

A) The evaluation of the dissertation is <b>POSITIVE</b>	This evaluation is assigned to a total number of at least 40 points	
B) The evaluation of the dissertation is <b>NEGATIVE</b>	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

As a member of the Scientific Jury and scientific supervisor of the doctoral studies, I give my positive assessment for awarding the educational and scientific degree "DOCTOR" to eng. MARIYA TSVETANOVA MONDASHKA in the scientific specialty 5.10. Chemical Technologies (Processes and Apparatus in Chemical and Biochemical Technology).

<b>07.04.2026</b>	The report was written by:	
date	<b>Ass. Prof. Ilonka Vasileva Saykova</b>	signature