R E P O R T

by Prof. Dr. **ALBENA DETCHEVA-TCHAKAROVA** (IGIC-BAS), member of the Scientific Jury on the PhD-thesis of the full-time doctoral student at the Analytical Chemistry Department at the Faculty of Chemistry and Pharmacy of Sofia University "St. Kliment Ohridski"

VALENTIN GEORGIEV GEORGIEV

Title: **“Methods for the determination of uranium in water and food”**

for the acquisition of educational and scientific degree " **doctor** "

Professional field: 4.2 Chemical Sciences (Analytical Chemistry)

Academic advisors: Prof. Dr. **IRINA KARADJOVA** and Assoc. Prof. Dr. **IVANKA DAKOVA**

The PhD-student **Valentin Georgiev Georgiev** was a full-time doctoral student at the Analytical Chemistry Department at the Faculty of Chemistry and Pharmacy of Sofia University "St. Kliment Ohridski". The title of his PhD-thesis is **“Methods for the determination of uranium in water and food”.** The dissertation contains 117 pages, including 18 figures and 28 tables. The bibliographic reference list covers 188 literature sources.

Uranium is one of the main contributors to the earth's natural radioactivity. The significant spread of this toxic element in the environment is due to the development of nuclear energy and the mining industry for the extraction of uranium. Human exposure to environmental uranium is considered a radiological health risk. Therefore a strict quality control of both the environment and the products intended for human consumption is needed. The analytical procedures for uranium determination should meet a number of requirements: to be fast and to allow determination in a wide concentration range; to ensure accurate results and to be applicable in routine analytical practice. The current PhD-thesis is focused on the possibilities for uranium determination by:

- Direct measurement of uranium concentration by ICP-MS, which includes the study of matrix interferences observed in the presence of macrocomponents in natural waters, as well as the possibility for their corrections and the ability to obtain accurate results.

- Determination of uranium after enrichment by solid phase extraction and instrumental measurement. A new sorbent - an ion imprinted polymer has to be synthesized and characterized for the selective concentration of uranium. Its application will allow the determination of uranium at low concentration levels by applying cheaper and more accessible instrumental methods than ICP-MS.

Because of the fact that the obtained results as well as the developed analytical procedures should be applied as routine in the laboratories controlling the uranium content, the following main tasks of the presented PhD-thesis have been formulated:

1. Application of ICP-MS for the determination of uranium in drinking, bottled, groundwater and surface water intended for human consumption;

2. Development of an analytical procedure for the selective enrichment of uranium with subsequent instrumental determination by ICP-MS and ICP-OES by means of synthesis and characterization of a new U(VI) ion-imprinted polymer providing high selectivity of uranium sorption.

Based on the presented studies and the results obtained from this research, the following **scientific and applied contributions** could be formulated:

1. An analytical method for the direct determination of uranium in natural waters by ICP-MS is developed by preliminary optimization of experimental parameters. The method is validated by comparative analysis using an alternative method based on the spectrophotometric determination of uranium, participation in an interlaboratory comparison and analysis of a certified reference material (river water). The extended uncertainty is evaluated at three concentration levels and the method is applied to determine the uranium content in mineral, drinking and groundwater from different regions in Bulgaria.

2. A novel U(VI) ion-imprinted polymer is synthesized and is used as a sorbent for the solid-phase extraction of U(VI)-ion. The synthesis procedure is relatively easy to perform, and the sorbent is characterized by high stability, low cost and ability to be reused. The newly synthesized sorbent exhibits high extraction efficiency for the target ion U(VI) under the optimized experimental conditions. The adsorption mechanism is also studied. It is proved that the sorption process proceeds as a surface monolayer on homogeneous binding sites, and the rate-limiting step is the formation of complexes between U(VI) ions and the chelating ligand 4-(2-Pyridylazo)resorcinol (PAR) incorporated into the polymer matrix.

3. A highly sensitive towards uranium content analytical procedure is developed for its determination in different types of natural waters, white, red and rosé wine, as well as in different monofloral honeys without preliminary digestion, based on solid-phase extraction with the newly synthesized sorbent and subsequent ICP-OES measurement. The accuracy of the results obtained is confirmed by further independent measurements.

On the PhD-thesis two scientific papers are published. The first of them is published in the highly renown international journal ***Molecules*** (IF_{2022}=4.6), quartile **Q1 – 25 points;** the other – in ***Comptes Rendus de L'Academie Bulgare des Sciences*** (IF_{2022}=0.3), quartile **Q3 – 15 points; altogether 40 points, required 30 points.** In both publications the PhD-student **Valentin Georgiev** is the first co-author which is a proof for his substantial contribution in the studies.

Parts of the PhD-thesis are presented on scientific meetings in Bulgaria and abroad – altogether 7 participations. The doctoral student is also participant in three scientific projects.

The scientific publications and the dissertation abstract correspond to the content of the PhD-thesis, the goals and tasks, the main results and the achievements. I have no critical remarks concerning the scientific and professional level of the doctoral student **Valentin Georgiev** as well as his PhD-thesis.

The PhD-thesis of the doctoral student **Valentin Georgiev** contains **scientific and applied results which are original contribution in science and meet all the requirements** of the Law for Development of Academic Staff in the Republic of Bulgaria and the Regulations for implementation of the Law for the development of the academic staff in the Republic of Bulgaria. Due to the above, I am convinced to give my **positive assessment** to the research presented by the above reviewed PhD-thesis, abstract, results and contributions, and I propose the esteemed scientific jury to award the educational and scientific degree **"Doctor"** to **Valentin Georgiev Georgiev** in the Scientific area: **4. Natural sciences, mathematics and informatics;** professional field **4.2. Chemical sciences**; Scientific specialty: **4.2. Chemical sciences (Analytical chemistry)**.

14.05.2024 Signature:

Prof. Dr. Albena Detcheva-Tchakarova