



REVIEW

of the materials submitted for participation in a competition for the academic position "Associate Professor" in the professional field 4.2. Chemical Sciences, scientific specialty "Analytical Chemistry (Instrumental Methods for Analysis)", announced in State Gazette issue 105 of 11.12.2020 for the needs of the University "Prof. Dr. Asen Zlatarov" - Burgas

Reviewer: Prof. Dr. Irina Karadjova, Faculty of Chemistry and Pharmacy, Sofia University "St. Kliment Ohridski "

The only candidate in the competition is chief assistant, Dr. Lenia Gonsalves. The presented materials are in full compliance with the requirements of the Law for Development of the Academic Staff in Republic of Bulgaria and the Regulations for its application, the Regulations for the Terms and Conditions for Acquiring Scientific Degrees and Occupying Academic Positions at University "Prof. Dr. Asen Zlatarov" - Burgas.

1. Brief biographical data about the candidate

Chief Assistant Dr. Lenia Gonsalves has graduated from the Faculty of Chemistry and Pharmacy at Sofia University as a Bachelor of Chemistry in 2003, and as a Master in 2005, Master's degree in "Modern Spectral and Chromatographic Method for Analysis". In the period 2008-2012 she has been a doctoral student at the Institute of Organic Chemistry with Center for Phytochemistry, BAS and the University of Hasselt, Belgium and she has finished her PhD degree with a qualification: Chemistry and Technology of Natural and Synthetic Fuels.

The scientific career of Chief Assistant Dr. Lenia Gonsalves has began at Organic Chemistry with Center for Phytochemistry, BAS, as a chemist and until 2015 she defended her doctorate and acquired the position of Chief Assistant. Her research interests are in the field of chemistry of solid fuels. Her research activity is related to the application of instrumental methods for analysis and characterization of coal - technical and elemental analysis, and chromatographic analysis of coal products. Since 2015, Dr. Leniya Gonsalves has been elected as Chief Assistant at the Central Research Laboratory (CNL) of the University "Prof. Dr. As. Zlatarov ", and since 2019 she has been a chief assistant at the Department of Chemistry of Faculty of Natural Sciences of the same university. During this period she has an active teaching activity and at the same time provides external analyses using instrumental methods in CNIL, related to servicing research activity at the University "Prof. Dr. Asen Zlatarov"; performing

2. Description of the submitted materials

Chief Assistant Dr. Lenia Gonsalves has attached a list of scientific papers for her entire creative period, a list and copies of the scientific papers which were presented for this competition, as well as a habilitation thesis. She is a co-author of a total of 43 publications, of which 21 have been published in journals with impact factor and impact rank. The number of observed citations of scientific papers according to Scopus data is 166. The list of 18 scientific publications were presented for participation in the competition, 16 of them were published in editions with impact factor and impact rank, one was published in international referenced and peer-reviewed edition (Web of Science) and one is published in a proceedings of scientific conference (Scopus). List of 72 citations for the period 2010-2017 are also included. About

70% of the candidate publications, presented in the competition, are published in journals from the first (6) and second quartile (4). The habilitation thesis includes results from 4 publications, published in Q1 journals.

The scientific results of the research studies have been reported at 30 scientific forums.

Chief Assistant Dr. Leniya Gonsalves has serious project activity - she has participated as a team member in 6 national projects, 1 international educational project and 6 international bilateral projects, one of which she has been a research supervisor.

A detailed reference for the teaching activity of the candidate is attached.

All submitted materials can be considered related to the topic of the competition. The candidate has attached a reference for the implementation of the minimum national requirements and the recommended criteria for holding the academic position "Associate Professor" in the scientific field "Natural Sciences, Mathematics and Informatics", professional field "Chemical Sciences" at the University "Prof. Dr. As. Zlatarov" - Burgas (Appendix 1). The distribution by indicators is as follows: indicator A - 50 points; indicator B - 100 points (recommended 100); indicator D - 228 points (recommended 200); indicator D - 144 points (recommended 100) and indicator E - 100 points (recommended 100). It is obvious that the Chief Assistant Dr. Lenia Gonsalves meets the requirements.

3. General characteristics of the candidate research activity and personal contribution.

Scientific contributions

Most of publications of Dr. Leniya Gonsalves are in the field of instrumental methods of analysis as methodological development and application, in the field of solid fuels as an interpretation of the results obtained and characterization of objects and processes. Probably from the point of view of an analyst, I would arrange in a different way than the candidate main directions in which research has been conducted and scientific contributions have been achieved:

- Development of new analytical methods, methodological development and adaptation of analytical methods.
- Interpretation of analytical results
- Characterization of different objects and obtaining new results for mechanisms and efficiency of processes.

However, this arrangement does not suppose homogeneous publications and their classification in the separate, defined directions. The publications presented for a review are in fact an amalgam of method development, interpretation of results, characterization of various objects and conclusions, which is exactly an example of interdisciplinary research. In line with the modern understanding of analytical chemistry which is not conducting of analyses, but precise development and application of new methods in order to obtain information for objects and processes I accept as a serious merit of the candidate's research.

Development of new analytical methods, methodological development and adaptation of analytical methods

Analytical methods has been developed and applied, based on Temperature Programmed Atmospheric Pressure Reduction (AP – TPR) and Temperature Programmed Atmospheric Pressure Oxidation (AP – TPO), realized as a hyphenated on-line method with gas chromatography with mass spectrometric detection (GC-MS) or as an off line system with

thermal desorption and GC-MS. The advanced detection variant allows to obtain reliable quantitative results for the content of chemical species of sulfur in different types of coal.

Appropriate optimization of instrumental parameters and development of new approaches, allowed the candidate to apply this analytical technique for qualitative and quantitative determination of the content of volatile organic compounds in other geological objects and thus to obtain reliable information about the composition of organic matter in them. The AP – TPR – TD – GC / MS method is optimized and applied for quantitative determination of a wide range of organic compounds in humic acids from Leonardite, humic acids from lignites “Maritsa Iztok” and “Stanyantsi

For the determination of elemental sulfur in coal, a new analytical method was developed, including extraction with CHCl_3 and subsequent HPLC (high performance liquid chromatography) analysis on the C18 reversed phase column. The developed new approach allows to obtain a more accurate balance of the different species of sulfur in coal.

A methodology for the quantitative determination of polyaromatic hydrocarbons in the composition of PM has been developed and validated. The developed methodology includes active sampling on quartz fiber filters and subsequent miniaturized ultrasonic extraction in a small volume of dichloromethane (10 ml). The obtained extracts were purified by column chromatography, further concentrated under nitrogen and PAHs were determined by GC-MS in SIM mode. Quantitative separation and determination of 19 compounds was achieved, the calibration was performed by the method of the internal standard (with 5 deuterated standards). The developed methodology is validated in terms of linear range, selectivity, limit of detection and quantification, precision and accuracy, i.e. is practically ready for application in the analytical practice of the EEA.

Within the scope of the research, a number of instrumental methods have been optimized and adapted as applications, such as thermal instrumental methods: thermogravimetry (TGA) and differential thermal analysis (DTA), UV-VIS, spectrophotometry, atomic emission spectrometry, which is also a significant scientific contribution.

Interpretation of analytical results.

The appropriate interpretation of the results from the AP-TPR and AP-TPO combined with GC-MS was used for: determination of the content of sulfur functionalities in coal and geological samples, evaluation of organic sulfur pollutants emitted during combustion of various commercial briquettes.

The appropriate combination of the results of the applied instrumental methods allows for reliable determination of the composition of the organic matter of different types of coal.

The interpretation of the results of AP – TPR – TD GC-MS of Leonardite determines a wide range of organic compounds in pyrolysates and on this basis results were obtained for the composition of humic acids - basic structural unit are 1-2 aromatic cycles condensed or bound, the presence of compounds with heteroatoms was also confirmed. The same approach was applied in the study of the composition of humic acids from lignites "Stanyantsi" and lignites "Maritsa East".

Interpretation of the results of TGA and DTA allows to determine the fuel characteristics of biodesulfurized coal and to prove the structural changes occurring during their oxidation.

The results for the content of PAHs in PM from urban ambient air in combination with the data on the mass concentrations of PM are interpreted in several aspects:

- Assessment of urban air quality as the content of PM and PAHs by comparison with the maximum allowable concentration and parameters that affect their changes.
- Assessment of the risk of cancer based on the measured concentrations.
- Assessment of the factors influencing the profile of PAHs. Interesting results have been obtained, showing that not only the source of PAHs determines their profile, but also the meteorological conditions and cross-border transmissions. Systematic studies have been conducted and important conclusions have been drawn for the distribution of the two fractions PM_{2.5} and PM₁₀. Higher homogeneity of PM_{2.5} distribution was observed in comparison to PM₁₀ in an urban atmosphere. Logical results were obtained for the influence of meteorological conditions on the mass concentrations of PM and PAHs associated in them. On this basis, reliable conclusions can be drawn about a common source of pollution, which in combination with PAHs profile would suggest also the nature of the source of pollution. In addition, the regression analysis performed showed a good correlation between the concentrations of PM_{2.5}, PM₁₀, and PAHs in them, which can also be used as evidence of a common source of pollution. Such conclusions based on a systematic research are extremely important for assessing the quality of the urban atmosphere and for objectively confirming the source of pollution.

Characterization of different objects and obtaining new results for mechanisms and efficiency of processes.

A significant part of the candidate's research (9 scientific publications) is dedicated to the biodesulfurization of coal, undoubtedly a topical area related to environmental protection, using efficient cleaning technologies. The developed analytical methods, the correct interpretation of the obtained results for the content of organic functionalities of sulfur in coal allowed the candidate to achieve complete and reliable characterization of the process of biodesulfurization of coal. The candidate expands and upgrades the research started in the PhD thesis for the influence of the coal matrix as a prerequisite for successful desulfurization and selection of a suitable microorganism for a certain type/rank of coal. Research is continuing with other biodesulfurization microorganisms for different-grade coal from the country. Important results for the degree of desulfurization depending on different parameters as well as the changes observed in the coal mine during bioprocessing have been obtained. As a final step, the impact of biodesulfurization on the fuel characteristics of coal was assessed. From a scientific point of view, the results of these studies clarify the mechanisms by which coal biodesulfurization takes place.

Appropriate instrumental methods (GC-MS) were applied for the characterization of mobile organic pollutants in Bulgarian lignites from the Thracian and Sofia coal basins, incl. mines "Maritsa East" and "Stanyantsi" after extraction at 25 °C with distilled water for 10 weeks.

The candidate demonstrates significant contributions to the possibilities for recovery and recycling of various biomass waste through thermochemical treatment aiming to obtain activated carbon, which has suitable adsorbent properties. The object of research are pig manure and tobacco biomass. Suitable conditions were found for the preparation of activated carbon from pig manure, which was characterized as a mixed micro-mesoporous material with good efficiency and high adsorption capacity toward Cr (VI) ions. The positive fact is that after the adsorption of the toxic form of Cr (VI) there is a reduction of Cr (VI) to the non-toxic specie

of Cr (III). The mechanism of adsorption has been established and the optimal pH 2 has been defined for carrying out the process, at which the concentration of Cr (III) in the solution is minimized.

Similar studies have been performed on biomass from three batches of tobacco used for soil bioremediation. Tobacco usually accumulates toxic elements and should not be composted or burned. In addition to the thermochemical treatment for the production of activated carbon, the experimental design also includes the analysis of mobile forms of the toxic elements in activated carbon in order to allow its further use as an adsorbent. Several extractants were used: water for the most mobile and soluble species of the elements; $\text{Ca}(\text{NO}_3)_2$ for the exchange forms; and NH_4Ac –EDTA for chelated complexes. The results show that only one of the tested samples is suitable for the production of activated carbon (the concentration of mobile forms of toxic elements in NH_4Ac – EDTA extract is below the detection limit), which can be used as an effective adsorbent for Cr (VI).

An approach has also been developed for the production of activated carbon from a thermoplastic polymer polystyrene by pre-oxidation with conc. H_2SO_4 and subsequent carbonization and activation. Two approaches of low temperature activation in the presence of air as an oxidant, contributing to the production of AB with acidic groups on the surface and activation with water vapor, leading to the production of AB with a well-developed microporous structure were compared. The influence of various parameters on the structure of resulting activated carbon and its adsorption activity toward Ni (II) in aqueous solutions were investigated. The mechanism of Ni (II) adsorption and the influence of pH have been studied in detail.

Thermal treatment of walnut shells in an inert atmosphere results in the production of biochar, classified as a microporous material. Experiments conducted on its extraction efficiency against Ni (II) show an ion exchange mechanism of adsorption and high efficiency. It can be used as an alternative to commercial biochars.

All publications of the candidate in the competition are collective. After the initial publications during the preparation of PhD thesis, the participation of Chief Assist. Dr. Lenia Gonsalves is essential in them. This gives me a reason to conclude that the personal contribution of the candidate in the most of the presented studies is undoubted and significant.

Scientific contributions can be characterized as new scientific results with very good practical application and potential final realization.

4. Reflection in the literature Chief Assistant Dr. Leniya Gonsalves has a list of citations of the scientific papers with which she participated in the competition and the general conclusion is that the research she conducts and publishes has found an echo in the literature. The articles dedicated to biodesulfurization have a significant number of citations and show the relevance of the obtained results. The publications related to the production of activated carbon from waste in just 4 years have 45 citations, which is a very good testament to the interest they have aroused.

5. Teaching activity

The teaching and pedagogical employment of the chief assistant Dr. Lenia Gonsalves is significant and diverse. She is already a lecturer of courses "Inorganic and Analytical Chemistry", "Modern Methods of Analysis" and "Modern Analytical Methods" and conducts exercises and seminars on "Organic Analysis";

6. Critical remarks

I have no general critical remarks on the research from the publications of Chief Assistant Dr. Lenia Gonsalves.

CONCLUSION Chief Assistant Dr. Lenia-Nezaet de Brito Gonsalves-Musakova participates in the competition with a set of publications that meets the requirements for the academic position of "Associate Professor" at the University "Prof. Dr. Asen Zlatarov "-Burgas in the professional field" Chemical Sciences ". The presented documents show that she is a productive young researcher in an interdisciplinary field, combining the development of instrumental methods and characterization of objects and processes. A review of the publications, without knowing the candidate personally, shows that after the initial participation in a working team in a promising scientific field, she has managed to build her own view and her own original ideas for future research. In this aspect, based on current and promising scientific topics, the quantity and quality of scientific papers, the response in the literature, scientific contributions, leadership and participation in research projects, as well as educational activities, I strongly recommend the Faculty Council of the Faculty of Natural Sciences to vote positively for the award of the academic position "Associate Professor" in the professional field 4.2. Chemical Sciences, scientific specialty "Analytical Chemistry (Instrumental Methods of Analysis)" to Chief Assistant Dr. Lenia Gonsalves.

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