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**Review of the doctoral dissertation of Jean Baptiste Baranyika, MSc, entitled:**

**"Application of isotope methods for determination of biocomponents in liquid fuels".**

**Introduction**

I prepared the presented evaluation of the doctoral dissertation of Jean Baptiste Baranyika, MSc, on the basis of Resolution No. 11/2024 of the Discipline Council of Earth and Environmental Sciences of the Silesian University of Technology on the appointment of reviewers of the doctoral dissertation dated 16 October 2024.

The discussed doctoral dissertation was prepared at the Silesian University of Technology in the Division of Geochronology and Environmental Isotopes under the supervision of Natalia Piotrowska, PhD, Eng, Professor at SUT. The review is to determine whether the submitted doctoral dissertation meets the conditions specified in Article 187 of the Act of 20 July 2018, Law on Higher Education and Science (Journal of Laws 2023, item 742, as amended), i.e. whether it presents the candidate's general theoretical knowledge in the discipline of Earth and Environmental Sciences and the ability to conduct scientific work independently, and whether it is an original solution to a scientific problem.

**Formal characteristics of the dissertation**

The reviewed dissertation consists of three published scientific articles:

1. Baranyika JB, Piotrowska N, Kłusek M, Michczyński A, Pawlyta J. 2022. *Testing the methods for determination of radiocarbon content in liquid fuels in the Gliwice Radiocarbon and Mass Spectrometry Laboratory*. Radiocarbon. 64(6);1447-1456. doi: 10.1017/rdc.2022.35.

2. Baranyika JB, Piotrowska N. 2023. *Determination of radiocarbon content in bio-oil samples by Mini Carbon Dating System in the Gliwice Radiocarbon and Mass Spectrometry Laboratory*. Geochronometrie. 50:21-27. doi:10.2478/geochr-2023-0005.

3. Baranyika JB, Piotrowska N, Michczynski A. 2024, *Determination of radiocarbon content in liquid fuel blends by accelerator mass spectrometry and liquid scintillation counting in the Gliwice Radiocarbon and Mass Spectrometry Laboratory*. Radiocarbon 66 (3): 437-447. doi:10.1017/RDC.2024.51.

The articles were published in English and are full-length research papers (i.e. they do not constitute short communications or polemics). In all three papers, the Doctoral Student is the first and corresponding author, and the accompanying co-authorship statements attest to his definitely leading role in the preparation of these publications (amounting to 75%, 80% and 80%, respectively). All articles were published in indexed scientific journals included in the Ministerial List (with a score of 140 points for Radiocarbon and 70 points for Geochronometry, respectively). The articles form a thematically coherent whole, all dealing with the title application of isotopic methods in the study of liquid fuel biocomponents and using three different research methodologies.

The articles are preceded by a preliminary description prepared in compatible language versions in English and Polish. The fact that the dissertation is written in two language versions by an English-speaking Doctoral Student is surprising to me (I understand that this is an intra-university legal requirement, but definitely not supportive of English-speaking dissertation supervisors). I will refer to the Polish language version in detail. The introductory description is 31 pages long and contains 6 chapters.

The introduction to the topic of the dissertation is divided into as many as four chapters: (1) description of the research topic, (2) scope of the research project, (3) significance of the dissertation and (4.1) objectives of the dissertation. I think that lesser fragmentation into individual chapters and better ordering of the content would have facilitated a better reception of the dissertation as a whole. Subsequently, in chapter 4.2, the Doctoral Student presents extended summaries of the scientific articles included in the dissertation. In chapter 5 he summarises his contribution to the whole dissertation project and chapter 6 is a summary of the obtained results.

Taking into account the information presented, I conclude that the dissertation submitted for review:

1) constitutes a collection of published and thematically related scientific articles;

2) contains an abstract in English and Polish;

Which means that it meets the formal requirements specified in Article 187 section (3) and (4) of the Act of 20 July 2018, Law on Higher Education and Science (Journal of Laws 2023, item 742, as amended).

**Substantive evaluation of the dissertation**

The dissertation presented for evaluation concerns the development and adaptation of methods for the analysis of 14C content in liquid fuels for the assessment of biocomponent content. The topic is presented quite clearly and concisely, although with some editorial shortcomings. The publications included in the dissertation are undoubtedly valuable documentation of newly developed or adapted measurement techniques, very well documented, which deserves special recognition. The development of analytical methods is usually the most arduous and labour-intensive aspect of work in the empirical sciences, also requiring a great deal of commitment and detailed knowledge of the undertaken subject matter. Therefore, I admire that during the short period of completing the dissertation the Doctoral Student managed to develop as many as three research methodologies, solidly document his measurement results and successfully publish them. However, while the publications themselves display a very good editorial and linguistic quality, the introductory part of the dissertation is written rather chaotically and would certainly benefit from better organisation of the content.

In the first chapter entitled “Description of the research topic”, the Doctoral Student explains the practical significance and legal requirements for increasing the use of biocarbon in fuels. He subsequently provides a very brief introduction to isotopic issues, limiting himself to very basic information. What I miss here is an introduction to the subject of 14C analyses, how the dating is done, how its decay proceeds and what is the half-life of this isotope – because its absence in fossil fuels follows directly from this, and that is unfortunately not clearly explained. Information on legal aspects is mixed in this chapter with the scientific basis of the research carried out. Subsequently, the author briefly describes the various measurement techniques for the determination of 14C content and introduces information on the required correction of isotopic fractionation. What is missing here is information on what isotopic fractionation is, why this correction is necessary and what is the role of stable carbon isotope measurements in this matter. As this is an important aspect of the measurement techniques discussed in this chapter, there should be a theoretical explanation of the process. The individual paragraphs of this chapter are not coherently and logically linked to each other, they start with very general content, and often lack a clear connection to the topic of the dissertation.

In the second chapter, "Scope of the research project", the Doctoral Student indicates the normative acts for the measurement methods he adapted, discusses the materials studied and which specific work was done within the scope of the dissertation. Finally, he mentions isotopic fractionation again, explaining briefly that this process can alter the final measurement results.

In the third chapter “Significance of the research”, the Doctoral Student discusses the reasons for the variability in the composition of the liquid fuels studied and explains the necessity of their detailed analysis and the adaptation of the methods commonly used for solid fuels. This chapter is very well and convincingly structured, although there could have been a smooth transition within the same chapter to the objectives of the work, which are only mentioned in the next chapter 4.

The objectives of the work are precisely defined: adaptation of the methods in the Gliwice Laboratory, determination of measurement uncertainties and understanding of potential causes of measurement errors in order to obtain more accurate and reliable results.

Subsequent chapters 4.2.1, 4.2.2 and 4.2.3 are extended summaries of the articles that constitute the dissertation, repeating the tables and figures which are also included in the articles. I think that here it would be sufficient to cite the relevant source in the article itself, which is after all a component of the dissertation. Below, I will concentrate on discussing the content of these component articles.

Article 1 (Baranyika et al., 2022) deals with the testing of methods for the determination of 14C content and quantification of biocarbon in liquid fuels by two methods: AMS and LSC. The paper describes in detail the sample preparation methods for both measurement techniques used. The reasons for the observed inconsistencies in the obtained carbon percentages are discussed in detail, while demonstrating the lack of influence of inconsistencies in quantification on the final result of 14C content. The article also discusses the methods for parallel stable isotope analyses of carbon 13C/12C used in the correction of isotopic fractionation. However, the results presented in Table 2 show that corrected and uncorrected results are not significantly different, so is it really necessary to perform this correction? The answer to this question is not discussed in the article.

Article 2 (Baranyika and Piotrowska, 2023) discusses the determination of 14C content in bio-oil samples using the Mini Carbon Dating System, a compact AMS analyser. Bio-oil and the biomass used in their production were analysed, allowing the results to be converted to the percentage of modern carbon in oil samples. The results of the analyses were meticulously presented and their precision was determined using appropriate statistical methods. It is interesting to note that the last bio-oil sample showed a higher pMC value than the original biomass used for production. This revealed a different origin of this sample, which shows the effectiveness of the performed analyses in answering practical questions about the actual origin of the bio-components in fuels.

Article 3 (Baranyika et al., 2024) deals with analyses of liquid fuel mixtures conducted with AMS and LSC methods. In this research, a background sample was used to correct the results of all analyses. The very good repeatability of the two measurement techniques used was demonstrated and a lower detection limit for both methods was determined. Also, in this paper, the precision of the measurements was tested in detail with appropriate statistical methods for processing the results.

What is missing throughout the dissertation is a synthesis of all the articles and the links between them, for example, was the MICADAS system discussed in Article 2 also used in Article 1, or is this a quite novel tool presented in Article 2 for the first time? The first article does not use this name, but the description of the sample preparation procedure is very similar, suggesting a likely application of the same procedure, however to different materials. Should the correction based on the background sample used in the last paper also be included in the previous results and in any future analyses? It would be helpful to summarise that the performed experimental measurements allowed the development of a specific laboratory procedure and indicated that specific aspects of the measurements made should be taken into account.

In Chapter 5, the Doctoral Student summarises his contribution to the overall research project in question, which is undeniably very significant, from the substantive and technical preparation to the performed analyses, the detailed processing of the data and their publication.

Chapter 6 briefly and substantially presents the conclusions, summarising the analysed samples and their results, the obtained measurement precision and a comparison of the two measurement methods: AMS and LSC.

All things considered, what is noteworthy in the entire dissertation is the number of samples analysed, considering their very labour- and time-consuming preparation and demanding measurements. The data has been very meticulously analysed and described, and the achieved measurement precision is very good, demonstrating the Doctoral Student's perfect mastery of the laboratory workshop.

Only the editorial side of the work, especially in the first chapters, could have been a little more polished. There are sometimes unspecific formulations and too far-fetched mental shortcuts, below are examples (which I also checked in the English version, where I found similar inaccuracies, so it is not the question of a faulty translation):

P. 7: "In contrast to the modern biosphere with high 14C concentrations, fossil fuels are devoid of this radioisotope due to their age (Dijs et al. 2006). This is why biofuels or fuel blends containing biocomponents are referred to as renewable fuels" - they are not renewable fuels because they have a high concentration of 14C, but because their resources are rapidly renewable. In my opinion, this topic should be explained in more detail here, there is not even basic information about the half-life of 14C and on what basis age estimation is performed using the 14C method. I think this should definitely be included in a dissertation on this topic.

P. 8: "In particular, CO2 emitted from the combustion of fossil fuels (…)” - The sentence is as if taken out of context, without relating information that these modern biofuels are produced by the assimilation of atmospheric CO2 whose characteristic 14C composition is due to local conditions.

Interchangeable use of the terms 14C and radiocarbon, once adopted nomenclature should be used throughout the work.

**Conclusion**

On the basis of the evaluation carried out, I consider that the submitted dissertation:

1) presents the Author's general theoretical knowledge in the discipline of Earth and Environmental Sciences, as evidenced by the elaborated review of the state of the art in methods of analysis of both radiocarbon and - stable isotopes, provided briefly in the introductory part of the dissertation, but also more extensively in the accompanying scientific articles;

2) demonstrates the ability to conduct research work independently - the Doctoral Student is the first and corresponding author in case of all three articles submitted for evaluation;

3) constitutes an original solution to a scientific problem - the author planned and performed all steps aimed at the determination of 14C in samples of liquid fuels: starting from factual preparation to the analysis of samples of various origins and with various preparation and measurement techniques, elaboration of their results, carrying out the appropriate statistical tests, evaluation of the precision of the analyses and, finally, recommendations regarding possible ways of preparation of various types of samples, the limit of detection and measurement possibilities.

In view of the above, I conclude that the doctoral dissertation submitted for evaluation by Mr Jean Baptiste Baranyika, MSc, entitled: "Application of isotope methods for determination of biocomponents in liquid fuels" meets the conditions specified in Article 187 of the Act of 20 July 2018, Law on Higher Education and Science (consolidated text: Journal of Laws of 2023, item 742, as amended) and I request that the Author be admitted to the further stages of the proceedings for the award of a doctoral degree in the discipline of Earth and Environmental Sciences.