FACULTY OF CHEMISTRY AND PHARMACY

Collegium Chemicum

ul. Oleska 48, 45-042 Opole

www.wch.uni.opole.pl

chemia(@uni.opole.pl

UNIVERSITY OF OPOLE

Prof. dr hab. inż. Piotr P. Wieczorek

e-mail: Piotr.Wieczorek@uni.opole.pl

Opole, 2025-01-12 

**REVIEW OF THE DOCTORAL DISSERTATION BY**

**Mr Jean Baptiste Baranyika, MSc,**

entitled

**“Application of isotope methods for determination of biocomponents in liquid fuels”**

The doctoral dissertation of Mr Jean Baptiste Baranyika, MSc, presented for evaluation, was carried out at the Department of Geochronology and Environmental Isotopic Research, Centre for Science and Education of the Institute of Physics, Silesian University of Technology, under the supervision of Natalia Piotrowska, PhD, Professor of SUT. Issues related to the development of effective analytical procedures for the determination of biocomponents in liquid fuels are the subject of the evaluated doctoral dissertation, which is the scope of research conducted by the research group of the dissertation supervisor.

The reviewed doctoral dissertation of Jean Baptiste Baranyik, MSc, performed under the supervision of Natalia Piotrowska, PhD, falls within this scope. Thus, the aim of this dissertation was to adapt the methodology for the determination of biocarbon content by isotopic methods used at the 14C and Mass Spectrometry Laboratory in Gliwice for the determination of biocomponents in liquid fuels by accelerator mass spectrometry (AMS) and using a scintillation counter (LSC method), to verify the accuracy of these procedures and to determine their uncertainty.

The assessed dissertation was not written in the classical dissertation layout and [but] in accordance with the regulations contained in the Journal of Laws of 2011, no. 84, item 455, art. 13(2) constitutes a thematically coherent collection of 3 papers published in prestigious international journals with a high impact factor (IF). The collection of papers is preceded by two summaries of professional accomplishments in English and Polish. The summaries are essentially 31-page monographs containing abstracts, lists of diagrams and abbreviations, a description of the research topic, the scope and significance of the work, the aim of the work, a description of the research and its results, details of which are included in the publications, a summary and statement of the author's contribution, general conclusions and a list of cited literature. This section is supported by 43 up-to-date and well-chosen citations from the literature. This is followed by copies of the publications included in the dissertation containing a detailed list of reagents and materials, research methods used, obtained results and figures and tables. All the papers forming the basis of the dissertation are multi-authored. Following each paper, the materials also include statements, in English and Polish, specifying the contribution, type of tasks and scope of work performed by the co-authors of the publication. These statements indicate that the contribution of the Doctoral Student was significant in these papers, both in the execution and in the preparation of the manuscripts of the publications. This is also indicated by the fact that in all these works, Jean Baptiste Baranyika, MSc, is both first and correspondence author.

Jean Baptiste Baranyika, MSc, began the implementation of his established research programme by testing the methods for the determination of biocomponents in liquid fuels used at the 14C and Mass Spectrometry Laboratory in Gliwice and by establishing their accuracy in the quantification of biocarbon in these fuels with both AMS and LSC methods. For the determination of the 14C carbon isotope, liquid fuel samples were combusted in an elemental analyser (EA) to obtain carbon dioxide, which was graphitised using H2 with iron powder as a catalyst. The graphite thus obtained was used to measure the carbon isotope with AMS. In contrast, the benzene method was used for the determination of 14C by the LSC method. In addition, 14C carbon concentrations in background samples (ON/UF-BC) were measured to determine the contamination of the samples with “modern carbon”. The reproducibility of the results during storage of the samples in sealed capsules was also checked and it was demonstrated that no change in carbon concentration was observed despite a loss of mass. It was shown that the results obtained with the use of the AMS and LSC methods are satisfactory and comparable. I have one comment, a question, to the presented research results. Why was only one result omitted from the calculation of the averages (Table l . sample B30, experiment 3) while in many cases the results differed by up to two times e.g. HVO sample, experiment 3. Please explain.

In the second paper (Paper 2), the Doctoral Student presented the results of a study of the 14C carbon content of various bio-oils measured with the use of the Mini Carbon Dating System (MICADAS), a state-of-the-art AMS system. Both the total carbon content and the content of the carbon isotope were determined in three different samples of oil obtained by catalytic depolymerisation of biomass, which was pistachio shells, and that biomass was used as a reference material. To obtain the graphite discs necessary in the 14C assay, a combustion procedure developed previously in EA was used to produce CO2, which was graphitised by a catalytic reaction in hydrogen with the use of iron powder as catalyst. The obtained results had good reproducibility, indicating that the sample preparation procedure used was appropriate. However, individual samples differed in their biogenic carbon content. A comparison of the values obtained for bio-oil 3 and the reference material indicated that only for sample 3 was the biocarbon content higher than that of the reference material, the reason for this being that the reference material dates from 2012 to 2016, while oil 3 probably dates from 1993 to 1994. Unfortunately, both in the summary of professional accomplishments and in the publication, I lack an attempt to present the reasons for this difference. Is it perhaps the result of nuclear explosions and/or the Chernobyl accident?

The next paper is a logical culmination of the conducted research, in which the Doctoral Student used the previously tested analytical procedures for the determination of carbon 14C isotope content by AMS and LSC methods, applying them to the analysis of carbon content in liquid fuel mixtures. Six fuel blends were obtained from hydrotreated vegetable oil (HVO) and a fuel supplied by an oil company (ON/UF-BC). For all prepared blends with different HVO contents, as well as for HVO and ON/UF-BC samples, radiocarbon content was determined by both methods. The results obtained for 14C carbon isotope were within the assumed uncertainty for both measurement methods and showed a linear dependence of the 14C concentration on the HVO content. In addition, the author examined the repeatability of the results obtained by the MICADAS spectrometer for 10 subsamples of the Blend-15 mixture and obtained good, consistent and reproducible results.

Given that the procedures developed and tested for the determination of biocarbon in various liquid fuels had good accuracy and repeatability, I believe that the dissertation presented for evaluation is a very interesting example of analytical work of potential practical importance. The results obtained allowed the author to conclude that the choice of method for carbon determination depends on factors such as sample size, age, desired precision and available capacity. The results of measuring the concentration of the 14C carbon isotope in fuel mixtures showed good repeatability with both the AMS and LSC methods. However, the LSC method is labour-intensive and requires a rather complicated procedure to prepare the sample for measurements, among other things, due to the need to convert samples to benzene. The AMS method, on the other hand, due to its greater sensitivity and precision, is better for analysing small samples. From the obtained results of tests of the 14C carbon isotope concentration in bio-oils and fuel blends, it can be seen that the AMS technique using the MICADAS spectrometer provides satisfactory accuracy and reproducibility, which, in my opinion, suggests the viability of application of this method in practice.

In my opinion, the summaries of professional accomplishments were very well prepared, with a comprehensive literature review of the subject and a detailed discussion of the results of the published studies. At this point, however, I have one comment. Analysing the materials provided, it is difficult to conclude that the Doctoral Student conducted a proper validation of the tested analytical procedures. In fact, he determined only the reproducibility and precision and gave the probable minimum detectability of the 14C carbon isotope in liquid fuels. Whereas, according to accepted analytical principles, a full validation of analytical methods should include determination of specificity, linearity, accuracy, limits of quantification and detection, precision, stability and flexibility. Such validation is, in my opinion, essential, in the context of the potential application of the developed procedures to commercial analyses which require accreditation.

I have no major reservations regarding the merits of the publications submitted for evaluation as a doctoral dissertation. This is because the papers were thoroughly assessed before publication by the relevant reviewers, especially as they were published in journals of high repute. It is noteworthy that the summaries of professional accomplishments are very well written and contain only a few minor spelling errors, which are not even worth mentioning.

In conclusion, I would like to state that the dissertation presented for review represents a high level of research and contains many elements of scientific novelty. The scope of the research, the experimental results contained in it, the manner of interpretation and inference indicate that Jean Baptiste Baranyika, MSc, has demonstrated the ability to conduct scientific research independently and has made a significant contribution to the development of research in the Earth and environmental sciences, especially analytical procedures which use isotopic methods utalitarian in the qualitative and quantitative determination of biocomponents in multicomponent mixtures such as liquid fuels. Having examined the dissertation of Jean Baptiste Baranyik, MSc, **I conclude that the presented disseratation meets all the requirements set forth in the Act on Academic Titles and Degrees for doctoral theses and I request its admission to further stages of the doctoral dissertation procedure.**