Professor Marek Krąpiec, PhD, eng. Kraków, 2025-01-31

Faculty of Geology, Geophysics and Environmental Protection

of the AGH University in Kraków

**Review of the doctoral dissertation by Komala d/o Aziz Gill, MSc, entitled “Application of isotope methods for determination of bio-based**

**content in solid materials”**

**Formal matters**

A letter dated 12.11.2024 from Mrs Natalia Piotrowska, PhD, Professor of SUT, Chairperson of the Discipline Council for Earth and Environmental Sciences at the Silesian University of Technology, in relation to the resolution of the above mentioned Discipline Council to appoint me as a reviewer in the proceedings on the awarding of the doctoral degree was the basis for the evaluation of the doctoral dissertation by Ms Komala d/o Aziz Gill, MSc.

I prepared my opinion in accordance with binding legal acts, on the basis of the provided documents (a summary of professional accomplishments, a list of published scientific works, copies of publications from the doctoral dissertation proceedings and statements of all co-authors of publications from the proceedings) and publications available in literature databases.

**Assessment of scientific achievements**

Ms Komala d/o Aziz Gill, MSc, presented a series of 4 original, thematically related publications as her doctoral dissertation:

* Gill KA, Michczyńska DJ, Michczyński A, Piotrowska N, Kłusek M, Końska K, Wróblewski K, Nadeau MJ, Seiler M. (2022). Study of bio-based carbon fractions in tires and their pyrolysis products. Radiocarbon. 64 (6): 1457-1469. DOI: 10.1017/RDC.2022.88.
* Gill KA, Michczyńska DJ, Michczyński A, Piotrowska N, Ustrzycka A. (2023). Technical carbon black and green technology. Geochronometria. 50 (1) : 250-256. DOI: 10.2478/geochr-2023-0016.
* Gill KA, Michczyńska DJ, Michczyński A, Piotrowska N. (2024), Monitoring of modern carbon fraction in disposable packaging. Radiocarbon, First View DOI: 10.1017/RDC.2024.35.
* Gill KA, Michczyńska DJ, Michczyński A. Bio-carbon content determination in disposable packaging by liquid scintillation counting. [in:] Werle S, Ferdyn-Grygierek J (red.) POB6 Monograph entitled: „Ochrona klimatu i środowiska, energetyka współczesna - wybrane zagadnienia" [*Climate and environmental protection, modern energetics - selected issues*], Silesian University of Technology (in press).

The selected publication output includes articles of which 3 were published between 2022 and 2024 and another has been accepted for publication. The articles included in the monograph series were published in very good and good Journal Citation Report (JCR) journals: *Radiocarbon* [items 1 and 3] and *Geochronometria* [item 2] and as a chapter in a scientific monograph published by the Silesian University of Technology [item 4]. The IF impact factor of the JCR-listed journals is within the range of 0.8 - 8.3 (350 points according to the Ministry of Science and Higher Education). In the evaluated collection, I identified one paper each with 3, 4 and 5 authors and one paper by 9 authors. In each of the papers listed, Ms Komala d/o Aziz Gill, MSc, was the first author and acted as the corresponding author. Complementary statements by the doctoral student and all co-authors are on file, showing that her own contribution ranged between 45 and 70 per cent and included the execution of all analytical steps from sample selection through benzene synthesis, sample graphitisation to elaboration and interpretation of results, as well as manuscript text preparation. I consider the selection of original publications for the concise series, [published] under the common title ‘*Application of isotope methods for determination of bio-based content in solid materials*’, to be correct and justified. All of the papers forming the basis of the dissertation have passed the peer-review process and meet the high requirements of reputable international journals, both in terms of content, language and editorial level. The level of all four publications is, in my opinion, correspondingly high.

The research conducted by the Doctoral Student focused on the determination of biocomponent content in the samples under scrutiny (e.g. tyre rubber and its pyrolysis products, disposable packaging materials and technical carbon black) based on the concentration of the 14C isotope in them. As stated by the Author, the objective of the doctoral dissertation was to develop, test and verify the methodology for the determination of biobased carbon content with the use of isotopic methods applied in the 14C and Mass Spectrometry Laboratory for solid samples that have not been covered so far by studies in that laboratory. The planned scope of work included: i. Determination of pretreatment requirements for the materials to be tested. ii. Development of an efficient methodology for the determination of 14C in various types of solid materials, which had not been previously studied, to be conducted with the use of liquid scintillation (LSC) and accelerator mass spectrometry (AMS) techniques. iii. Determination of 14C concentrations in the studied solid materials. iv. Development of efficient protocols for the determination of biobased carbon. I consider the cited scope of research as ambitious, while the choice of research topic itself as very pertinent and interesting.

Publication 1 (Radiocarbon 64(6):1457-1469) presents the results of biocarbon concentration measurements in tyres and their pyrolysis products obtained by two techniques (AMS and LSC) in three different laboratories. Pyrolysis oil samples of recovered carbon black were analysed at the 14C Mass Spectrometry Laboratory in Gliwice (LSC and AMS) and the National Laboratory of Age Determination in Trondheim, Norway. The IRMS method was used to calculate the isotopic fractionation correction for the LSC measurements. The rubber samples were analysed at the 14C Mass Spectrometry Laboratory in Gliwice with the use of the LSC technique only and at the National Laboratory of Age Determination in Trondheim, Norway, with the use of the AMS technique. Therefore, the study was also a form of inter-laboratory comparison, which showed good agreement between the obtained results. An interesting finding was provided by the results of 14C isotope concentrations in pyrolysis oil and soot. The values were dependent on the participation of truck tyres in the pyrolysed mass, where larger truck tyre content resulted in higher 14C concentration values.

Paper no. 2 (Geochronometria 50(1): 250-256) presents the results of tests conducted on technical carbon black samples with different degrees of fineness and specific surface area. They were analysed by two radiocarbon techniques (LSC and AMS) at the 14C Mass Spectrometry Laboratory in Gliwice. The low 14C concentration values in the TCB samples are indicative of their production from fossil materials. The study also provided an intra-laboratory comparison, demonstrating the reliability of using LSC and AMS techniques to measure 14C isotope concentrations in TCB samples. For some samples, statistical inconsistencies were observed between the results obtained by LSC and AMS techniques. This was probably due to the inhomogeneity of the samples.

Publication 3 (Radiocarbon, DOI: 10.1017/RDC.2024.35) determined the fraction of modern carbon in samples of disposable packaging made from: paper, wood, sugar cane and wheat bran. In that study, samples were analysed with the use of the radiocarbon AMS technique at the 14C and Mass Spectrometry Laboratory in Gliwice. The samples were analysed in two batches. In the first batch, a small random portion was analysed, while in the second batch the samples were analysed in layers, with the exception of paper and wood (cutlery) samples. All samples appeared to be contemporary, as they showed 14C isotope concentrations above 100 pMC. Samples made of paper showed 14C concentrations between 100 and 112 pMC, while samples of wooden cutlery had results ranging from just over 114 to about 136.5 pMC. Samples made from sugar cane and wheat bran had the lowest 14C concentration values, which are almost equal to the current 14C concentration values in the atmosphere, indicating that the material originated from modern plant crops. The obtained results (in 4 out of 10 cases) proved the need to homogenise a larger sample volume to obtain a result representative of the tested DPM batch.

In paper 4 (Monograph POB6, Bio-carbon content determination…) 14C concentration and the amount of bio-carbon were determined with the use of the LSC technique. Packages from the same batch as for the AMS measurements in the third publication were used for the LSC measurements. The measurements which utilised the LSC technique also indicated the contemporary origin of the tested samples, however, it was observed that in some cases there were differences between the AMS and LSC measurements, which were greater than within single uncertainties. Considering inhomogeneity of the samples taken from a large batch of test material and applying the recommendation of the EN16640 standard to assume the uncertainty of the determination of biochar in a sample at 3%, the LSC and AMS results were found to be consistent within a single uncertainty for 8 cases and within a double uncertainty for 2 cases.

The performed research allowed for the development of measurement procedures for new types of samples not previously analysed at the Gliwice Laboratory. It was determined that no preliminary chemical preparation is required.

The significance of sample homogeneity for accurate measurements is an important conclusion of the study. Simple carbonisation was found to be insufficient for homogenisation; therefore, future studies should utilise full combustion in a vacuum setup to prevent the loss of light carbon and reduce isotopic fractionation.

The total output of the Doctoral Candidate includes 9 scientific articles published in journals listed in the JCR database and a scientific monograph. In addition to the papers constituting the monograph series, Ms Komala d/o Aziz Gill, MSc, is a co-author of 5 other multi-author publications. All publications from the JCR list were published between 2022 and 2024.

Another form of disseminating research results is their presentation at national and international conferences, in which the PhD student participated several times, resulting in 8 poster presentations..

Ms Komala d/o Aziz Gill, MSc, completed internships at the University of Sevilla (Spain) and the Norwegian University of Science and Technology in Trondheim.

In conclusion, I positively evaluate the scientific activity of the Doctoral Candidate translated into the output in the form of published papers in thematic periodicals of worldwide circulation. In the course of completing her doctoral studies, the Candidate has deepened her skills both in the area of the experimental research performed and the method of elaboration of the results, as evidenced, among other things, by the publication series and the prepared guide paper.

**Final evaluation**

In my opinion, the reviewed doctoral dissertation deserves an unequivocally positive assessment. It has been performed on the basis of rich and properly collected material and analysed in detail, taking into account properly selected methods. The achieved results are interesting and valuable, the interpretation of the obtained results is correct and the conclusions are adequately documented.

My evaluation of the scientific research conducted within the doctoral programme of Komala d/o Aziz Gill, MSc, presented in the four publications constituting the basis of the doctoral dissertation is definitely positive. The Doctoral Candidate undertook a research topic that is, in my opinion, important and showed competence in the selection of research methods. I consider the research results to be valuable and making a new contribution to science.

The presented series of publications fulfils the usual requirements for doctoral dissertations as well as the statutory ones, which is why I request that Komala d/o Aziz Gill, MSc, be admitted to the further stages of the doctoral programme.