THE AGH UNIVERSITY OF KRAKÓW

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**REVIEW OF THE DOCTORAL THESIS by Komal d/o Aziz Gill, MSc entitled: "Application of isotope methods for determination of biocomponents in solid materials", performed under the scientific supervision of Danuta J. Michczyńska, PhD, Professor of the Silesian University of Technology in Gliwice**

**1. Basis for the review**

The letter of Natalia Piotrowska, PhD, Professor of SUT, Chairperson of the Discipline Council for Earth and Environmental Sciences of the Silesian University of Technology dated 12.11.2024 (based on the resolution of the Discipline Council for Earth and Environmental Sciences of the Silesian University of Technology dated 16.10.2024 on the appointment of reviewers of the doctoral thesis) is the basis for the review of the doctoral thesis of Ms Komal d/o Aziz Gill.

**2. Introduction**

The use of isotopic methods in the analysis of biocomponent content of solid materials is an important tool to accurately distinguish between fossil and biogenic materials. The basis of this technology is the difference in the carbon 14C isotope content in organic materials. 14C isotope is present in living organisms in a fixed proportion relative to other carbon isotopes, it decays by beta-ray emission and has a half-life of approximately 5730 years. 14C carbon atoms are formed in the atmosphere at a constant rate, which means that the ratio of 14C to 12 C remains almost constant over time. This is because 14C atoms enter living organisms as 14CO2 through photosynthesis and digestion and then leave the organism through respiration and excretion processes, and also due to the decay of nuclei. If an organism dies, there is no exchange of carbon with the environment, but the 14C nuclei inside the organism continue to decay with a constant half-life, and the ratio of 14C to 12C decreases. Analysis of the exchange of the 14C to 12C ratio can be used to estimate the time elapsed since the death of the organism. Analytical techniques which use isotopic methods include accelerator mass spectrometry (AMS) and liquid scintillation spectrometry (LSC). The use of isotopic methods for the determination of bio-based carbon is governed by EN 16640:2017 standard ("*Bio-based products Bio-based carbon content - Determination of the bio-based carbon content using the radiocarbon method.*”)

Current research, as well as waste management policies in line with a circular economy, require the use of modern analytical methods, including isotopic methods. Isotopic methods are used primarily in the packaging industry, in recycling and waste management and in the energy sector. However, it should be emphasised that the research which uses isotopic methods is still limited due to the high cost of the equipment, the need to maintain an adequate laboratory and the technological sophistication of these methods (highly qualified personnel is required to operate and interpret the results).



In view of the above, I believe that the thesis addresses an extremely modern, up-to-date and important research topic concerning the assessment of biobased carbon content in a variety of materials associated with everyday use. Faced with increasing environmental challenges and the need to reduce the use of fossil raw materials, the Doctoral Student conducted comprehensive analyses of a wide range of waste materials, i.e. tyre rubber, its pyrolysis products, disposable packaging materials and technical carbon black. Using advanced analytical techniques such as accelerator mass spectrometry (AMS) and liquid scintillation technique (LSC), the work provides valuable scientific data to support the development of sustainable materials and technologies. I conclude that the topic and research interests undertaken by the Doctoral Student are fully justified, well thought-out, go beyond the average scientific research and, above all, demonstrate knowledge of current issues and challenges in the area of waste management.

In my opinion, Komal d/o Aziz Gill's doctoral thesis entitled: "The use of isotopic methods for the determination of bio-component content in solid materials" is an important contribution to both the development of scientific knowledge and its practical application. The issues addressed are not only topical, but also perfectly in line with contemporary environmental challenges and the pursuit of sustainable development. The use of isotopic methods to analyse the content of bio-components responds to the growing need to promote materials with lower environmental impact, making this work relevant in many fields.

**3. Evaluation of the thesis topic and scope**

The doctoral thesis by Komal d/o Aziz Gill, MSc, was realised at the 14C and Mass Spectrometry Laboratory of the Institute of Physics - the Centre for Science and Education of the Silesian University of Technology. The laboratory mainly conducts research involving radiocarbon and isotopic analyses in interdisciplinary applications, including age determination and research on new areas and materials, such as bio-carbons. Owing to the use of the accelerator mass spectrometer (MICADAS), research capabilities have been significantly enhanced, including analyses of 14C isotope concentrations in solid samples.

The doctoral thesis presented for review consists of an extended abstract in English and Polish and three scientific articles published in JCR-listed journals and a chapter in a scientific monograph of the Silesian University of Technology.

In the abstract of the thesis, which is a series of thematically related articles, the Doctoral Student carefully described the scope of the work as well as the aims and theses of the research. The main objective of the thesis was to develop a methodology for the determination of biobased carbon with the use of isotopic methods. She also stated four specific objectives comprising primarily the development of an initial preparation, a detailed methodology for the determination of 14C using LSC and AMS techniques, followed by the determination of the concentration of 14C in the materials studied and the development of protocols for the determination of biobased carbon. The Doctoral Student's single thesis is that the concentration of biobased carbon can be determined using the 14C isotope measurement method, indicating that this is in accordance with EN 16640 standard.

Then, in the chapter "Description of the subject of the research", she presented: i) the characteristics of the carbon isotope 14C (Subchap 3.1), ii) the importance of the radiocarbon method in the determination of biobased materials, (Subchap. 3.3) and (iii) the chapter on waste treatment (Subchap. 3.4). In my opinion, Subchap. 3.4 does not contain relevant information on waste treatment methods and waste management. This is important from the point of view of the waste treatment products obtained and their further application. In the last part of Chapter 3, the Doctoral Student presented an inventory of the samples analysed in the work. She analysed a wide range of waste materials of various types, i.e. pyrolysis oils, rubber, disposable materials (plates, cups, cutlery, etc.) and technical carbon black. I believe that the stated aim and scope of the thesis are correct, and that focusing scientific attention in the area of research that makes it possible to distinguish samples produced from contemporary materials (e.g. obtained by thermochemical processing of waste) from those produced from fossil fuels is important in both cognitive and utilitarian terms.

In chapter 5, the Doctoral Student describes the methodology of the conducted research. Within the framework of her work, she conducted research using two isotopic techniques, i.e. liquid scintillation counting (LSC) and accelerator mass spectrometry (AMS), and applied mass spectrometry of isotopic ratios to determine the isotope correction fractionation for samples investigated by the LSC technique. In the description of the methods, the author pointed out the advantages of the isotopic techniques used and described in detail the methodology of the measurements performed. It should be noted that some of the waste materials were studied by the Doctoral Student at the National Laboratory of Age Determination in Trondheim, Norway, during a research internship.

Chapter 6 constitutes the main part of the thesis, in which the Doctoral Student presents the results and conclusions of her research, which she published in a thematic series. The publication series includes the following:

1. 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.
2. Gill KA, Michczynska DJ, Michczynski A, Piotrowska N, Ustrzycka A. (2023). Technical carbon black and green technology. *Geochronometria* 50 (1): 250-256,
3. Gill KA, Michczynska DJ, Michczynski A, Piotrowska N. (2024). Monitoring of modern carbon fraction in disposable packaging. *Radiocarbon* 66 (5): 1032-1040.
4. Gill KA, Michczyńska DJ, Michczyński A, Bio-carbon content determination in disposable packaging by liquid scintillation counting. Werle S, Ferdyn-Grygierek J (eds) POB6 Monograph "*Climate and environmental protection, modern energetics - selected issues*", Silesian University of Technology.

"*Radiocarbon*" is an international scientific journal, published by Cambridge University Press, containing articles in the field of isotopes and techniques used in archaeological, geophysical, oceanographic and related dating. "*Geochronometria*" is a scientific journal of the Silesian University of Technology publishing papers in radiocarbon dating, isotopic methods and others.

In publication I, the Doctoral Student shows that used tyres, which, when untreated, cause environmental pollution, can be a valuable material with a wide range of applications. The paper presents a detailed method for determining the concentration of the radiocarbon isotope (14C) in tyres and their pyrolysis products. Three pretreatment methods and two isotopic techniques were used in the study. It was shown that the 14C concentration values were dependent on the amount of truck tyres pyrolysed. Furthermore, 14C concentration was found to be higher in pyrolysis oil compared to rubber and higher in truck tyres than in passenger car tyres.

Publication II includes the analysis of technical carbon black (TCB) to determine the 14C concentration and biobased carbon content to verify the origin of the materials from which they were obtained. Carbon black samples with different degrees of granularity and specific surface area were selected for the study. From the tests conducted, it was found that the technical carbon black samples analysed contained a low concentration of the 14C isotope <1 pMC, confirming that these materials were either not produced from renewable sources or were produced with a minimal involvement of those.

In publication III, the Doctoral Student presented the possibility of using isotopic techniques in the research of disposable packaging of organic origin made of materials, i.e. paper, wood, sugar cane and wheat bran. It is very important to undertake the analysis of this type of material, as single-use packaging waste represents a very large part of municipal waste that can be thermochemically treated according to the circular economy assumptions. Within the analyses carried out, results were obtained which indicated a high concentration of 14C, i.e. above 100 pMC, confirming that the packaging was made from bio-waste and not fossil materials. However, due to the wide variety of tested materials and the number of samples analysed, it was difficult to systematise the obtained test results. There is also a lack of information on whether or how the results obtained can contribute to the selection of raw materials for the production of, for example, disposable plates or cups.

Publication IV, which is a chapter of the Monograph "*Climate and Environmental Protection, Modern Energy - Selected Issues*", presents research on the biocarbon content of disposable packaging conducted with the use of the LSC method. The publication of research results from the application of isotopic techniques in this monograph was most appropriate, as the monograph constitutes valuable scientific material, covering key topics related to climate and environmental protection and modern energy. This work provides up-to-date information, research results and analyses of waste management taking into account the assumptions of a closed loop economy and sustainable development.

Summarising the above achievements of the Doctoral Student in the form of a series of publications, it should be added that she also presented the results of her research at international and national scientific conferences. The internship at the National Laboratory of Age Determination in Trondheim, Norway, is an important element of her scientific development and testifies to the high level of her research. Thanks to international cooperation (University of Seville, Spain), she was able to acquire new knowledge and practical skills in state-of-the-art research methods such as isotopic analysis.

While assessing the thesis from an editorial point of view, I find that it has been carefully prepared, according to accepted standards for doctoral theses. The thesis is clearly divided into an introductory part, a description of the methodology (particularly relevant in this thesis), a summary of the main research results and conclusions, and publications that constitute a thematic series. A section on plans for further research is missing. Each chapter is coherent and logically linked to the previous ones. Sometimes, however, a broader presentation of the topic, e.g. a discussion of the state of the art concerning the application of isotopic methods in waste or biocarbon research, would have been desirable. The language of the publication is correct. The author uses appropriate specialist terms. The thesis contains a list of tables, figures and abbreviations.

**3. Evaluation of the thesis**

I evaluate the presented thesis positively. The doctoral thesis of Komal d/o Aziz Gill, MSc, entitled "*Application of isotopic methods for the determination of bio-components in solid materials*" constitutes a significant contribution to the development of scientific knowledge in the field of material research that uses isotopic techniques. The topic undertaken by the Doctoral Student is demanding and complex, as it concerns the use of advanced isotopic techniques for the precise determination of bio-components in solid materials. Such analyses require a broad knowledge of isotopic chemistry, environmental chemistry, materials science and waste treatment issues. In addition, it is experimental work that required laboratory skills and, above all, operation of specialised research equipment such as accelerator mass spectrometer (AMS) and liquid scintillation systems. Performing such research requires precision, experience and the ability to interpret results at a level that allows reliable and innovative conclusions to be formulated. The Doctoral Student has demonstrated that she possesses such qualities. In addition, her internships and international collaborations have contributed to broadening and consolidating her knowledge of isotopic techniques.

I consider the main achievements of the Doctoral Student to be:

* Development of a measurement methodology using the LSC technique for materials not previously analysed such as rubber, disposable materials made of paper, wood and sugar cane and wheat bran and carbon black.
* Development of a methodology for graphitisation of pyrolytic oil and recovered soot samples.
* Preparation of samples for the determination of δ13 C by IRMS in order to determine the correction of isotopic fractionation for the results of 14C concentration in samples analysed by the LSC technique
* Performance of comparative tests in other laboratories.

Some observations, questions and comments came to me while reading the paper. Here are the most important of these:

1. In the “Description of the subject of the research”, the state of the art presented regarding the application of radiocarbon methods to the study of waste-type materials is very sketchy. Has this type of research been carried out by other researchers? If so, what was their scope? Please provide a broader overview of the issue.
2. What thermochemical waste treatment methods are used for the materials analysed by the Doctoral Student? Please discuss.
3. What was the criterion for selecting the materials for the study (Table 1)? Are there other types of materials that could also contribute relevant information in terms of biobased carbon content?
4. What physical and chemical parameters of waste materials are important in isotopic studies? Which ones facilitate and which ones hinder the preparation of material for testing and subsequent analysis?
5. The Doctoral Student showed that for tyre samples she obtained a large scatter of results. How should the material be prepared for testing so that the results are consistent? Maybe some kind of pre-treatment should be used?
6. Based on your research and analysis, can you conclude that both AMS and LSC techniques can be used for all types of samples, or are there any limitations?
7. The study concluded that no initial chemical preparation was required, with the exception of washing with demineralised water. Are there situations where a more advanced preparation would be necessary?
8. The Doctoral Student has done comparative studies in other laboratories. Did she observe any differences in the results?
9. Based on the research carried out, does the Doctoral Student believe that the current EN 16640:2017 European Standard limits or facilitates the interpretation of results in the context of the variety of materials analysed? Are there areas where this standard needs to be modified or updated?
10. How can the obtained results be used in practice, for example in the context of waste treatment and the use of their products, i.e. biocarbon or bio-oils? What environmental benefits might arise from the wider use of isotopic methods in the analysis of the materials investigated in this thesis?

I would like to emphasise that the above comments are of a debatable nature, they do not detract from the scientific value of the reviewed work and I hope that they will be a starting point for the discussion of the details of the work during its public defence and will motivate future research directions of the Doctoral Student.

**5. Summary**

The doctoral thesis of Ms Komal d/o Aziz Gill, MSc, submitted for review, responds to the important scientific challenge of using isotopic methods to determine the content of bio-components in solid materials, which is in line with current research trends on waste management in accordance with sustainable development and environmental protection. The Doctoral Student has demonstrated scientific maturity by clearly defining the aim of the work, carefully planning and carrying out a very advanced experimental study. The analysis of the obtained results was performed in a reliable manner and summarised with conclusions that are of significant cognitive as well as practical importance. The presented research results represent an original solution to a scientific problem and can be applied in the economic and social sphere.

During the course of her research work, Ms Komal d/o Aziz Gill has demonstrated that she has a sound theoretical knowledge in the discipline of Earth and Environmental Sciences (especially in terms of applied isotopic methods and their practical applications), as well as the ability to conduct scientific research independently. In addition, the Doctoral Student has effectively utilised advanced research technologies and international standards, further highlighting her high level of research competence.

I am convinced that the reviewed doctoral thesis of Ms Komal d/o Aziz Gill, MSc, entitled: "Application of isotopic methods for the determination of bio-components in solid materials" meets the conditions and requirements for doctoral thesis defined in Article 187 of the Act of 20 July 2018. - Law on Higher Education and Science. **In view of the above, I make a motion to the Discipline Council for Earth and Environmental Sciences of the Silesian University of Technology to admit the Doctoral Student to the next stages of the doctoral procedure**.