ORIGINAL ARTICLE

Effective Atomic Number based on Energy Dispersive X-Ray (EDX) Analysis and Carbon Hydrogen Nitrogen (CHN) Analysis for Phantom Material in Medical Physics Applications

Siti Hajar Zuber[1], Nurul Ab. Aziz Hashikin[1], Mohd Fahmi Mohd Yusof[2], Rokiah Hashim[3], Mohd Zahri Abdul Aziz[4]

[1] School of Physics, Universiti Sains Malaysia, 11800, Penang, Malaysia.
[2] School of Health Sciences, Universiti Sains Malaysia, 16150, Kelantan, Malaysia.
[3] School of Industrial Technology, Universiti Sains Malaysia, 11800, Penang, Malaysia.
[4] Advanced Medical and Dental Institute, Universiti Sains Malaysia, 13200, Penang, Malaysia.

ABSTRACT

Introduction: In medical physics applications, effective atomic numbers are often employed to set apart and specify the interaction of ionizing radiation with matter. **Methods:** The effective atomic number of soy-lignin bonded with *Rhizophora spp*. particleboards were analyzed using Energy Dispersive X-ray analysis and Carbon Hydrogen Nitrogen Analyzer. The effective atomic number were compared and recorded with reference to the effective atomic value of water. **Results:** The result showed that the effective atomic number calculated for adhesive bound *Rhizophora spp*. samples were close to effective atomic value of water, with 3.34 – 3.47 % differences by using Energy Dispersive X-ray and 6.47 – 6.78 % differences by using Carbon Hydrogen Nitrogen analysis. The result revealed that through Energy Dispersive X-ray method, the effective atomic number was much closer to water compared to Carbon Hydrogen Nitrogen analysis. **Conclusion:** Despite the availability of hydrogen content in the samples in Carbon Hydrogen Nitrogen analysis, Energy Dispersive X-ray method was much more preferred and gave better result compared to Carbon Hydrogen Nitrogen analysis thus provide a compelling argument for the use of Energy Dispersive X-ray method to measure the effective atomic number of *Rhizophora spp*. particleboard in medical physics applications.

Keywords: Effective atomic number, Tissue-equivalent phantom, *Rhizophora spp*

Corresponding Author:
Nurul Hashikin Ab. Aziz, PhD
Email: hashikin@usm.my
Tel: +604-6533670

INTRODUCTION

The effective atomic numbers (Z_{eff}) are often utilized to characterize the interaction of ionizing radiation with matter. Z_{eff} calculation in any composed materials showed the relationship between the cross-section diverse radiations interaction with the matter and the atomic numbers of the constituent elements in the composed material (1–6). Since the X-ray was first introduced and widely used in medical applications including diagnostic and therapy, knowledge on dosimetry became one of the utmost importance in medical fields (7). Photon interaction parameters including effective atomic number are required in order to provide details on photon association with target material especially in radiation study, and particularly important for the material to be used as phantom (8).
Phantom is any material that can represent soft tissue of human and an important tool in radiotherapy dosimetry. Water has been acknowledged by IAEA as a standard phantom and it has been used universally in radiotherapy. Water is presented with reproducible radiation properties and widely available, thus it is recommended for dosimetry purposes in radiotherapy. Given the importance of organ dose calculation in radiotherapy treatment, tissue-equivalent phantom medium mimicking human body anatomy should be a focus target for more refined study in term of dose and treatment setting.

It is well-known that water is acknowledged as a good medium to represent human body due to its properties, and water also exhibit excellent measurement for radiation absorption and scattering in radiation and dosimetry study. However, due to its physical characteristics and non-solid state, many commercialized phantoms replaced water for dosimetry study, which include polystyrene, acrylic and wood-based phantom (9). Commercially available but expensive anthropomorphic phantoms which is RANDO phantom (Alderson Research Labs, Stanford, CA) and recently, the ATOM® phantom (CIRS, Norfolk, VA), are often used for dosimetric radiation measurements.

Effective atomic number is closely related to attenuation properties of materials towards ionizing radiation. If a material has Z_{eff} value close to water, it is said to have similar attenuation properties to water (10,11). *Rhizophora spp* is becoming more prominent in the study of phantom for radiation study, can be found growing abundantly in the coastal area in Malaysia. At photon energy of 59.54 keV, the study had found that *Rhizophora spp.* wood provides the closest mass attenuation coefficient and mass density to water, with linear attenuation coefficient of 0.0212 mm^{-1} compared to 0.0205 mm^{-1} of water which allows the initiation of further investigation of this particular type of wood. High agreement within 2 % of PDD using Co-60 photon energy was also reported (12). Further investigation on binderless particleboard of *Rhizophora spp.* was done due to its tendency to warp and split over time (13,14). Adhesives are indispensable components in wood composites as they can physically and mechanically affect the properties of wood composites. Phenol-formaldehyde (PF) has conquered the wood industry over the years as the commercial adhesive, however, natural adhesive were preferred over petroleum-based adhesive due to its health concern (15). Natural-based soy flour and lignin were chosen in this study as adhesives bonded with *Rhizophora spp.* Based on previous study, lignin as single adhesive material is inferior when compared to mixture of lignin with other natural-based adhesives (16). The strength and water resistance of wood composite improved when combined with formulation of lignin and other natural adhesive (16).

This study focused on the calculation of effective atomic number for adhesive-bonded *Rhizophora spp.* based on the elemental composition using Energy Dispersive X-ray analysis (EDX) and Carbon Hydrogen Nitrogen (CHN) analysis. EDX methods were used extensively in the previous study, and the outcomes were close to the target value, which was close to the effective atomic value of water (17–19). However, there is another method of measuring the elemental composition in a material which is by using Carbon Hydrogen Nitrogen (CHN) Analyzer. CHN Analyzer often used to provide a means for the rapid determination of nitrogen, carbon and hydrogen in organic materials. Oxygen composition in the material, although were not calculated in the process, can be determined arithmetically based on the result obtained. However, this particular method is rarely used and reported in the previous study, thus this study will utilize both methods to obtain the elemental composition of the elements on the samples, and the results were compared. The outcome of this study may reveal the preferred method between EDX and CHN in the analysis of elemental compositions and effective atomic number which are particularly important to characterize a phantom material in medical physics applications.

MATERIALS AND METHODS

Sample preparation

For this study, slabs of particleboards at the dimension of (23 x 23 x 0.5) cm^3 were prepared with *Rhizophora spp.* as raw material with natural-based lignin and soy flour as adhesive materials. All the samples were prepared at a target density of 1.0 $g \cdot cm^{-3}$ at different adhesive percentages, 0 %, 6 % (4.5 % soy flour and 1.5 % lignin) and 12 % (6 % soy flour and 3 % lignin) by using hot pressing at approximately 200 °C, with pressure of 20 MPa for the duration of approximately 20 minutes. The measurement of *Rhizophora spp.* particles, adhesive materials used and water for the fabrication of the particleboard were calculated according to previous study (20,21) and defined by Equation 1.

$$\rho = M/V; \rho=1\ g.cm^{-3}$$
$$M_R = W_R\% \times \rho \times (1+ MC\%_R)$$
$$M_S = W_S\% \times \rho V \times (1+ MC\%_S)$$
$$M_L = W_L\% \times \rho V \times (1+ MC\%_L)$$
$$M_W = 7\% \times \rho V - [(M_R \times MC\%_R) + (M_S \times MC\%_S) + (M_L \times MC\%_L)]$$

[Eq. 1]

where ρ, ρ_t, M, and V are the density ($g \cdot cm^{-3}$), target density ($g \cdot cm^{-3}$), approximate mass (g), and volume (cm^3) of the board, respectively. Parameters M_R, $M_R\%$, and $MC\%_R$ are the approximate mass (g), weight percentage (%), and moisture content (%/L) of *Rhizophora spp.* wood particles. The variables M_S, $W_S\%$, and $MC\%_S$ are the approximate mass (g), weight percentage (%), and moisture content (%/L) of soy flour. M_L, $M_L\%$, and $MC\%_L$ represented approximate mass (g), weight percentage (%), and moisture content (%/L) of lignin. Variable MW is the approximate mass (g) of water used in the formulation. For EDX study, the samples were cut into 5.0 x 5.0 mm^2 whereas for CHN analysis, the samples were prepared in powder form. Soy flour and lignin were also prepared separately for both EDX and CHN analysis.

Effective atomic number using EDX analysis

EDX was employed to dictate the elemental fraction of each samples, which were first coated with platinum for conductivity. SEM-EDX NOVA NANOSEM 450 in NORLab, School of Physics, Universiti Sains Malaysia, was used for this study. The samples were then fixed onto specimen holders and examined under vacuum condition using SEM. The Z_{eff} is measured using Equation 2.

$$Z_{eff} = [\sum_{i=1}^{n}(e_i z_i^m)]^{\left(\frac{1}{m}\right)}$$

[Eq. 2]

Where e_i and z_i are electron fraction and atomic number of i^{th} element in the sample respectively. m is fixed value of 3.4 which represents the hypothetical coefficient for water and biological matters. The electron fraction of the i[th] element can be measured using Equation 3.

$$a_i = \frac{fw_i\left(\frac{z_i}{A_i}\right)}{\sum fw_i\left(\frac{z_i}{A_i}\right)}$$

[Eq. 3]

Where fw_i and A_i are fractional weight and atomic mass of the i[th] element respectively.

Effective atomic number using CHN Analyzer

Carbon Hydrogen Nitrogen (CHN) Analyzer was used to record the composition of elements in the samples. The analysis was performed using The Perkin Elmer 2400 Series II CHN Elemental Analyzer, Universiti Sains Malaysia. Percentage fraction of element H, C and N were provided by the analysis, whereas for O, the percentage was calculated based on the results. The Z_{eff} was measured using Equation 1. A paired sample T-test using Microsoft Excel 2019 application was performed to compare the effective atomic number calculated based on the elemental fractionation determined by EDX and CHN methods.

RESULTS

Z_{eff} based on EDX analysis

The effective atomic number of *Rhizophora spp.* particleboard bonded with natural-based lignin and soy flour was shown in Table I (22). Table II displayed the Zeff value calculated and Z_{eff} of the previous study compared with water (17,23). The Z_{eff} value for 0 %, 6 % and 12 % adhesive-bonded *Rhizophora spp.* samples were 7.1622, 7.1724 and 7.1759, respectively. The Z_{eff} value for soy flour is 7.1226 and for lignin is 6.9041 which was determined through EDX method.

Table I: Fractional weight calculated using EDX method.

Sample	Elemental weight in fraction, w_i			
	H	C	O	N
A_0	-	0.484	0.484	0.032
A_6	-	0.474	0.486	0.041
A_{12}	-	0.477	0.492	0.031
Soy flour	-	0.467	0.437	0.096
Lignin	-	0.613	0.355	0.031

A = approximately 0 – 103 μm particle sizes
0 = binderless; 6 = 6 % adhesives; 12 = 12 % adhesives

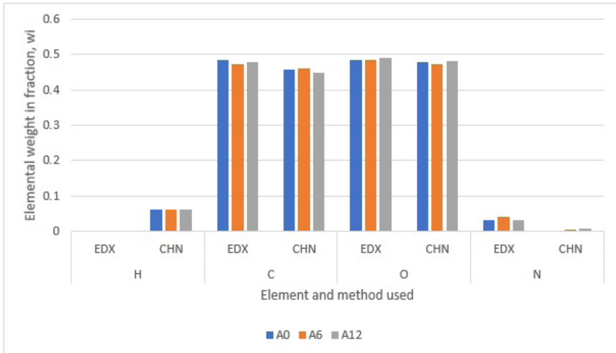
Z_{eff} based on CHN analysis

The effective atomic number for *Rhizophora spp.* particleboard bonded with natural-based lignin and soy flour was calculated and determined by using CHN analysis. The CHN analysis, elemental composition for carbon, hydrogen and nitrogen were obtained, and oxygen content was calculated arithmetically from the result, shown in Table II (20). The comparison between the fractional elemental weight for *Rhizophora spp.* samples using EDX and CHN methods at different percentages of adhesives were shown in Figure 1.

Table II: Fractional weight calculated using CHN analysis.

Sample	Elemental weight in fraction, w_i			
	H	C	O	N
A_0	0.063	0.458	0.478	0.001
A_6	0.063	0.460	0.472	0.005
A_{12}	0.062	0.449	0.482	0.007
Soy flour	0.064	0.407	0.455	0.075
Lignin	0.058	0.600	0.339	0.004

A = approximately 0 – 103 μm particle sizes
0 = binderless; 6 = 6% adhesives; 12 = 12% adhesives



A = approximately 0 – 103 μm particle sizes
0 = binderless; 6 = 6% adhesives; 12 = 12% adhesives

Figure 1: Comparison of fractional elemental weight of the samples using EDX and CHN methods. The comparison was made between *Rhizophora spp.* samples bonded with different percentages of soy flour and lignin as adhesives.

Table III showed the Z_{eff} value for all the samples obtained from CHN analysis (24,25). The effective atomic number for 0 %, 6 % and 12 % adhesive-bonded *Rhizophora spp.* samples were 6.928, 6.917 and 6.9403, respectively. The Z_{eff} value for soy flour is 6.9384 and for lignin is 6.6596 which was determined through CHN analysis method. A paired sample t-test was performed to determine the statistical significance of both methods used in this study. The p-value obtained from the paired sample T-test was less than 0.05, revealing that CHN method used in the measurement of effective atomic number did statistically give significant differences in comparison to the EDX method.

DISCUSSION

Previous studies that investigated the effective atomic number for phantom-based materials often used EDX method instead of CHN analysis (13,19,26). The Z_{eff} obtained for adhesive bonded with *Rhizophora spp.* sample investigated using EDX method were also closer to Z_{eff} value of water, with a difference in value

Table III: Comparison between Z_{eff} calculated based on CHN Analyzer and EDX analysis.

Sample	Z_{eff} (CHN)	Z_{eff} (EDX)
[a]A_0	6.928	7.162
[a]A_6	6.917	7.172
[a]A_{12}	6.940	7.176
[a]Soy flour	6.938	7.123
[a]Lignin	6.660	6.904
[b]A_0	-	7.180
[b]Tannin bonded	-	7.220
[c]Corn starch bonded	-	7.590
Water	7.420	

A = approximately 0 – 103 µm particle sizes
0 = binderless; 6 = 6 % adhesives; 12 = 12 % adhesives
[a]Current study, [b]Yusof (2017), [c]Hamid (2018)

within 3.34 % to 3.47 % compared to CHN analysis with difference in value within 6.47 % to 6.78 %. Nonetheless, some studies did utilize CHN method due to its ability to detect hydrogen element. Table III showed the comparison between Z_{eff} calculated based on CHN Analyzer and EDX analysis. A factor that may attribute to the differences is the sample preparation, for EDX, the samples were in dry, solid slab form whereas, for CHN, the samples were in powdery form. Different methods of analysis were performed by both EDX and CHN Analyzer. For EDX, the elemental composition was determined by using X-ray technique and relied on the interaction of the sample with radiation. The relative abundance and chemical properties of a sample can be determined by using EDX. However, the sample is coated with a metallic substance such as platinum or gold in order to make it conductive, which may affect the sample with impurities. Although the layer was able to reduce the thermal damage, improve the secondary signal and avoid the production of distorted images, the presence of impurities may reduce the efficacy and quality of result obtained. For CHN Analyzer, the method to obtain the elemental composition, with the addition of catalysts requires an oxygen-rich environment. Other than that, the process also demands a high-temperature combustion procedure based on the classical Pregl-Dumas method. The addition of catalysts to aid the conversion process may cause impurities and reduce the accuracy of result obtained (27,28). CHN analyzer is often acknowledged as the most direct purity analysis despite the main drawbacks of CHN analysis which includes the requirements for accurate weighing of 1.0 to 2.0 milligram of sample and the fact that samples are usually run as an automated batch rather than on an individual sample basis. Despite the advantages and drawbacks for both EDX and CHN analysis methods, the results showed better result by using EDX, and this method also much more preferred compared to CHN analyzer, which may be due to its availability.

CONCLUSION

The result of the effective atomic number determined by EDX and CHN analysis showed close value to Z_{eff} of water. The EDX method, which was preferred compared to CHN analysis may be due to the availability of the analyzer itself. Despite the availability of hydrogen content in the samples in CHN analysis, EDX method was much more preferred and the corresponding Z_{eff} value of the particleboard showed a fascinating favorable similarity to water compared to CHN analysis. This finding hence proposed a higher value-added use of *Rhizophora spp*. bonded with natural-based soy flour and lignin as possible phantom material with the measurement of Z_{eff}.

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REFERENCES

1. Issa SAM, Susoy G, Ali AM, Tekin HO, Saddeek YB, Al-Hajry A, et al. The effective role of La2O3 contribution on zinc borate glasses: radiation shielding and mechanical properties. Appl Phys A [Internet]. 2019;125(12):867. Available from: https://doi.org/10.1007/s00339-019-3169-5
2. Alatawi A, Alsharari AM, Issa SAM, Rashad M, Darwish AAA, Saddeek YB, et al. Improvement of mechanical properties and radiation shielding performance of AlBiBO3 glasses using yttria: An experimental investigation. Ceram Int [Internet]. 2020;46(3):3534–42. Available from: https://www.sciencedirect.com/science/article/pii/S0272884219329189
3. Issa SAM, Darwish AAA, El-Nahass MM. The evolution of gamma-rays sensing properties of pure and doped phthalocyanine. Prog Nucl Energy [Internet]. 2017;100:276–82. Available from: https://www.sciencedirect.com/science/article/pii/S0149197017301634
4. Uosif MAM, Mostafa AMA, Issa SAM, Tekin HO, Alrowaili ZA, Kilicoglu O. Structural, mechanical and radiation shielding properties of newly developed tungsten lithium borate glasses: An

experimental study. J Non Cryst Solids [Internet]. 2020;532:119882. Available from: https://www.sciencedirect.com/science/article/pii/S0022309319307525

5. Issa SAM, Ahmad M, Tekin HO, Saddeek YB, Sayyed MI. Effect of Bi2O3 content on mechanical and nuclear radiation shielding properties of Bi2O3-MoO3-B2O3-SiO2-Na2O-Fe2O3 glass system. Results Phys [Internet]. 2019;13:102165. Available from: https://www.sciencedirect.com/science/article/pii/S2211379719305820
6. Tekin HO, Issa SAM, Kavaz E, Altunsoy Guclu EE. The direct effect of Er2O3 on bismuth barium telluro borate glasses for nuclear security applications. Mater Res Express [Internet]. 2019;6(11):115212. Available from: http://dx.doi.org/10.1088/2053-1591/ab4cb5
7. Kurudirek M. Effective atomic numbers and electron densities of some human tissues and dosimetric materials for mean energies of various radiation sources relevant to radiotherapy and medical applications. Radiat Phys Chem [Internet]. 2014;102:139–46. Available from: http://www.sciencedirect.com/science/article/pii/S0969806X14001613
8. Khan FM, Gibbons JP. Khan's the physics of radiation therapy. Lippincott Williams & Wilkins; 2014.
9. Banjade DP, Tajuddin AA, Shukri A. A study of *Rhizophora spp* wood phantom for dosimetric purposes using high-energy photon and electron beams. Appl Radiat Isot. 2001;55(3):297–302.
10. Tur□ucu A, Demir D, Ll̲nder P. Effective atomic number determination of rare earth oxides with scattering intensity ratio. Sci Technol Nucl Install. 2013;2013.
11. Duvauchelle P, Peix G, Babot D. Effective atomic number in the Rayleigh to Compton scattering ratio. Nucl Instruments Methods Phys Res Sect B Beam Interact with Mater Atoms. 1999;155(3):221–8.
12. Bradley DA, Tajuddin AA, Sudin CWACW, Bauk S. Photon attenuation studies on tropical hardwoods. Int J Radiat Appl Instrumentation Part A Appl Radiat Isot. 1991;42(8):771–3.
13. Marashdeh MW, Hashim R, Tajuddin AA, Bauk S, Sulaiman O. Effect of particle size on the characterization of binderless particleboard made from *Rhizophora spp.* Mangrove wood for use as phantom material. BioResources. 2011;6(4):4028–44.
14. Marashdeh MW, Bauk S, Tajuddin AA, Hashim R. Measurement of mass attenuation coefficients of *Rhizophora spp.* binderless particleboards in the 16.59–25.26keV photon energy range and their density profile using x-ray computed tomography. Appl Radiat Isot [Internet]. 2012;70(4):656–62. Available from: http://www.sciencedirect.com/science/article/pii/S0969804312000097
15. Ferdosian F, Pan Z, Gao G, Zhao B. Bio-based adhesives and evaluation for wood composites application. Polymers (Basel). 2017;9(2):70.
16. Nasir M, Gupta A, Beg MDH, Chua GK, Kumar A. Physical and mechanical properties of medium-density fibreboards using soy—lignin adhesives. J Trop For Sci. 2014;41–9.
17. Yusof MFM, Hashim R, Tajuddin AA, Bauk S, Sulaiman O. Characterization of tannin-added *Rhizophora spp.* particleboards as phantom materials for photon beams. Ind Crops Prod [Internet]. 2017;95:467–74. Available from: http://www.sciencedirect.com/science/article/pii/S0926669016307427
18. Yusof MFM, Hamid PNKA, Tajuddin AA, Abdullah R, Hashim R, Bauk S, et al. Characterization and attenuation study on tannin-added *Rhizophora spp.* particleboard at high energy photon and electron. In: AIP Conference Proceedings. AIP Publishing; 2017. p. 40002.
19. Taghizadeh Tousi E, Hashim R, Bauk S, Suhaimi Jaafar M, Abuarra H, Mohammad A, et al. Characterization of the rhizophora particleboard as a tissue-equivalent phantom material bonded with bio-based adhesive. Maderas Cienc y Tecnol. 2015;17(2):305–18.
20. Zuber SH, Hashikin NAA, Mohd Yusof MF, Hashim R. Physical and Mechanical Properties of Soy-lignin Bonded *Rhizophora spp.* Particleboard as a Tissue-equivalent Phantom Material. Bioresour Vol 15, No 3 [Internet]. 2020; Available from: https://ojs.cnr.ncsu.edu/index.php/BioRes/article/view/BioRes_15_3_5558_Zuber_Soy_Lignin_Bonded
21. Tousi ET, Hashim R, Bauk S, Jaafar MS, Abuarra AMH, Ababneh B. Some properties of particleboards produced from *Rhizophora spp.* as a tissue-equivalent phantom material bonded with Eremurus spp. Measurement [Internet]. 2014;54:14–21. Available from: http://www.sciencedirect.com/science/article/pii/S0263224114001547
22. Zuber SH, Hashikin N, Mohd Yusof MF, Hashim R. Lignin and Soy Flour as Adhesive Materials in the Fabrication of *Rhizophora spp.* Particleboard for Medical Physics Applications. J Adhes.
23. CWA CWS. Kayu Tropika Sebagai Bahantara Setaraan Tisu Untuk Kajian Dosmteri. M. Sc. Thesis, Universiti Sains Malaysia; 1993.
24. Yusof MFM, Hamid PNKA, Tajuddin AA, Hashim R, Bauk S, Isa NM, et al. Fabrication and characterisation of phantom material made of Tannin-added *Rhizophora spp.* particleboards for photon and electron beams. In: Journal of Physics: Conference Series. IOP Publishing; 2017. p. 12036.
25. Hamid P, Mohd Yusof MF, Hashim R, Tajuddin A. Characterisations and attenuation properties of corn starch-bonded *Rhizophora spp.* particleboards as water equivalent phantom material at 16.59-25.26 XRF photons and 99mTc gamma energies. Int J Environ Eng. 2018 Jan 1;9:254.
26. Yusof MFM, Hamid PNKA, Tajuddin AA, Hashim R,

Bauk S, Isa NM, et al. Mass attenuation coefficient of tannin-added *Rhizophora spp*. particleboards at 16.59–25.56 keV photons, and 137 Cs and 60 Co gamma energies. Radiol Phys Technol. 2017;10(3):331–9.
27. ASTM. ASTM D5291: standard test methods for instrumental determination of carbon, hydrogen and nitrogen in petroleum products and lubricants. In ASTM West Conshohocken; 2010.
28. Committee A. Evaluation of analytical instrumentation. Part XIX CHNS elemental analysers. Accredit Qual Assur. 2006 Nov 1;11:569–76.