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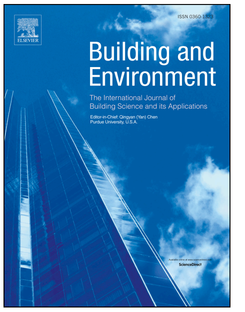

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PII: S0360-1323(22)00494-2

DOI: https://doi.org/10.1016/j.buildenv.2022.109259

Reference: BAE 109259

To appear in: *Building and Environment*

Received Date: 23 March 2022

Revised Date: 27 May 2022

Accepted Date: 1 June 2022

Please cite this article as: Marć M, Rutkowska Mał, Hejna A, Barczewski M, Biocomposites from recycled resources as candidates for laboratory reference material to validate analytical tools used in organic compounds emissions investigation, *Building and Environment* (2022), doi: https://doi.org/10.1016/j.buildenv.2022.109259.

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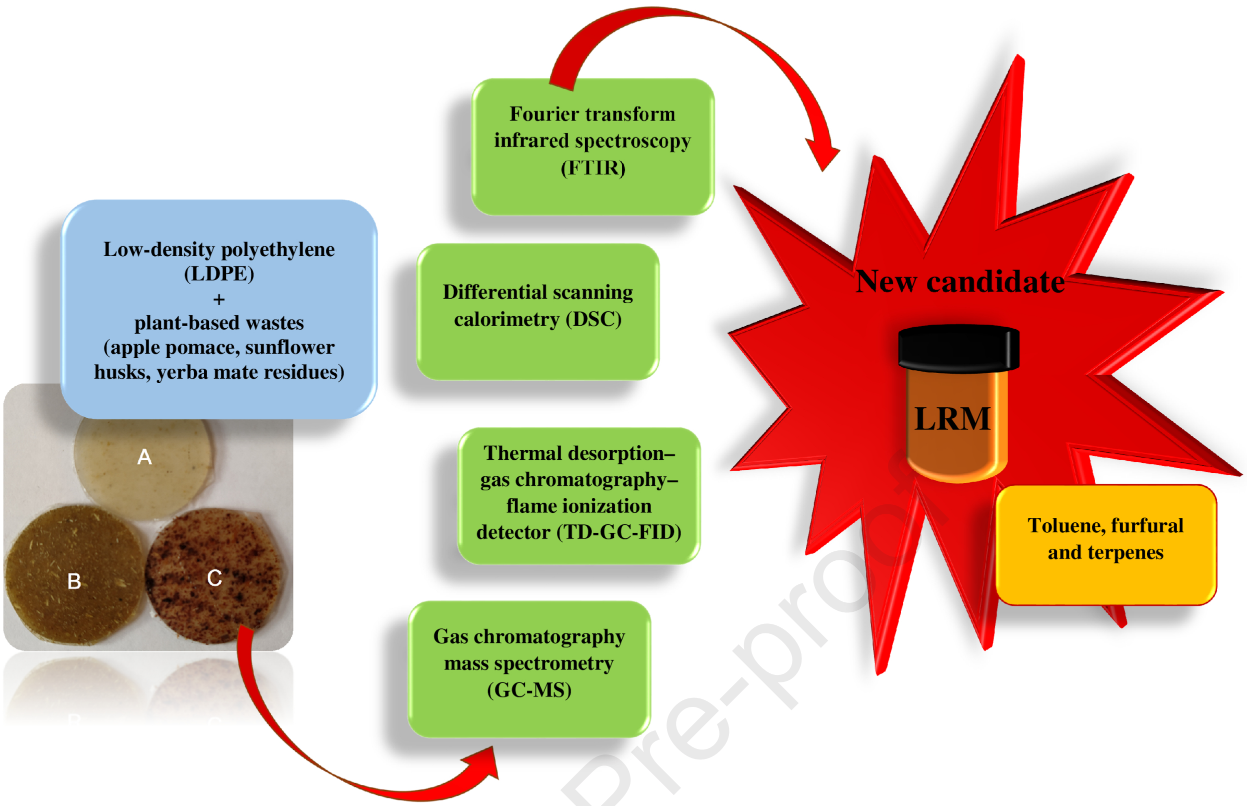

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Biocomposites from recycled resources as candidates for laboratory reference material to validate analytical tools used in organic compounds emissions investigation

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Abstract

A suitably chosen reference material should meet specific criteria like representing one of the compound classes most commonly occurring in indoor materials as well as having optimal long-term stability during storage and transport to its destination point and having a compact size. The described interdisciplinary pilot research was aimed to develop and characterize a polymer-based candidate for the laboratory reference material (LRM) of selected representatives of monoaromatic hydrocarbons (toluene and furfural) and terpenes emissions. Recycled, petroleum-based low-density polyethylene (LDPE) was applied as a matrix and was filled with plant-based wastes, such as apple pomace (AP), sunflower husks (SH), or yerba mate (YM) residues. The performance and suitability of the developed candidate for use as laboratory reference material was analyzed using FT-IR spectroscopy and differential scanning calorimetry (DSC). The migration potential of the representatives of monoaromatic hydrocarbons and terpenes emitted from the developed polymer material was assessed using the stationary emission microchamber system (µ-CTE 250). In the case of candidates for LRM with the addition of YM and AP, a clear relationship was observed between the samples seasoning time in the chamber and the total amount of VOCs released into the gaseous phase, including identified and determined representatives of terpenes. Furthermore, the existence of a clear relationship between the size (intensity) of the emission defined by the calculated summary parameters (TVOCs and sum of terpenes) and the seasoning/conditioning temperature of polymeric materials with bioadditives was observed.

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Keywords: reference material; indoor materials; product emissions testing; emissions; bioadditives; terpenes

1. Introduction

Following the International Union of Pure and Applied Chemistry (IUPAC), the primary alternative for testing the accuracy of an analytical method is to analyze a certified reference material (CRM) [1]. Nevertheless, it is not easy to obtain a CRM with the same or similar matrix as the sample analyzed. According to the Committee on Reference Materials of the International Organization for Standardization, a reference material is one that is "sufficiently homogeneous and stable with respect to one or more specified properties, which has been established to be fit for its intended use in a measurement process" [2]. CRMs should be similar to real samples in terms of the composition of the matrix, levels of analytes, potential interferences, and the material's physical state [3]. In addition, generally available CRMs have a high price due to time-consuming and costly certification steps. In the absence of a suitable CRM, an alternative strategy is to use a reference material (RM), also known as a laboratory reference material (LRM) or laboratory control material (LCM) that must also meet the same homogeneity and stability criteria to provide suitability. Such materials can be used at all steps of the measurement process, from instrument calibration, validation of analytical methods, and the quality control process [4].

Synthetic materials can contain many chemical additives and contaminants that can migrate and contaminate food, water, soil, and air. Among other things, volatile organic compounds (VOCs) contained in plastic-based materials can be released into the air at ambient temperatures due to their high vapor pressure. Specialized laboratory equipment, such as emission test chambers, allow samples to be characterized under conditions that mimic the indoor environment [5]. However, there is a lack of a proven method or analytical tool to assess the precision of the results obtained employing the stationary emission chamber (dynamic headspace analysis) or automatically headspace system (static headspace analysis). Only a few solutions are known in which the suitability of the designed and used analytical devices measuring emissions of organic compounds are studied with non-commercial laboratory-made RMs. The published solutions are mainly based on a predefined quantity of toluene – research associated with the new type of diffusion-controlled RM for VOCs emission studies. The thin film of synthetic homogeneous material made of polymethyl pentene (PMP) was used as a carrier medium. Then selected organic compound – toluene was loaded to the PMP carrier medium structure through a diffusion process. A described analytical tool might be considered a representative or

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substitute for a "dry" building or constructing material in the emission studies. Besides, it should be noted that diffusion-controlled RM using PMP as a carrier medium was the main subject of the pilot inter-laboratory research project, which contains four participating laboratories [6, 7]. A different solution was associated with the preparation and characterization of a tool defined as a liquid-inner tube diffusion-film-emission (LIFE). The LIFE was prepared based on the following elements: (i) a cylindrical container made of Teflon; (ii) a thin diffusion film (membrane) made of aluminum oxide melamine-impregnated paper as a cover and (iii) liquid – a solution of a single purified organic compound representing VOCs. The device was designed to assess the working parameters (the performance) of stationary emission chambers (for both large-scale and small-scale chambers) applied to estimate organic compounds' emission rate from furniture materials. The proposed solution was an easily-used analytical tool with a constant emission rate of toluene under defined temperature and relative humidity conditions [8, 9]. An example of another approach is thermoplastic material (polyurethane) as a carrier for selected VOCs. Thermoplastic polyurethane is a specific carrier coated with VOCs. The coating is conducted under increased pressure to ensure optimal penetration of VOCs to deeper layers of the carrier material [10].

A comparison of data achieved employing two different analytical devices or methods for determining the type and quantity of chemicals released from indoor materials is not an easy process. Very often, there is no explicit statistically significant agreement between the emissions of contaminants released from the same studied material. Differences between the results are primarily attributed to the fact that these devices operate in different analytes sampling modes. Dissimilarities between results may also be directly caused by the investigated indoor material's characteristics, composition, superficial structure, and precise storage/conditioning time at the retailer's premises. Because most indoor materials are characterized by varying degrees of homogeneity, it is expected that by using two different analytical devices or methods, statistically significant differences will be found for the obtained data [11, 12]. One solution that would allow for comparing research results acquired using the different methodological approaches and showing the potential differences is to introduce a suitable prepared LRM characterized by a constant predefined emission profile of selected chemical compounds. This option would allow a detailed comparison and indicate the analytical device offering better precision and accuracy [13, 14]. An adequately chosen LRM should meet specific standards like being neutral to elements of the sampling device, and the specific compound or defined group of chemicals ought to be released from the developed LRM at a predefined rate in a predefined time interval. Because the complicated testing procedure

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employed various types of devices classified as the emission chambers, LRMs for the quality assurance of the organic compounds emissions research are required [8, 9, 13, 14]. Consequently, the challenge for interdisciplinary research centers is to develop and characterize the new types of LRMs containing a valuable tool in the field of estimating the chemical compounds emissions from representatives of various types of indoor and building materials. In the indoor environment, VOCs might be emitted directly to the gaseous phase by building materials (e.g., bricks, breezeblocks, paints, and impregnates) as well as from household equipment (furniture, floor coverings, wide spectrum of electronic equipment, wallpapers, textiles). Many of mentioned materials or equipment's contain or consist entirely of a polymer matrix [11, 13]. Consequently, the challenge for interdisciplinary research centers is to develop and characterize the new types of LRMs containing a valuable tool in the field of estimating the chemical compounds emissions from representatives of indoor materials containing polymeric matrix. Prospective application of LRM might contain an alternative solution for both long-term emission chamber investigations (under dynamic conditions in constant flow rate) as well as mathematical calculations to perform model predictions of characteristics of emission rate of volatile and semi-volatile organic compounds (SVOCs) [8]. Li [15] demonstrate and describe the mass-diffusion mathematically–physics model suitable for three different VOCs emission stages - predicting organic emissions in early, midterm, as well as late stages. Mathematical calculations were performed based on the results obtained with the use of two reported small environmental-chamber investigations [15].

The main objective of this study was to develop and fully characterize the candidate for LRM with its morphological characteristics and preliminary emissions profile (specific emission rate) of representatives of monoaromatic hydrocarbons (toluene and furfural - a compound derived from the added fruit wastes [16]) and terpenes. Investigations were performed depending on the temperature conditions and seasoning time (defined as a storage time of a material sample inside the emission chamber under given conditions of humidity, temperature and gas flow rate). The novelty of performed interdisciplinary research was that proposed candidates for LRMs were prepared based on commonly used low-density polyethylene (LDPE), and plant-based wastes (originated from the food industry – apple pomace, sunflower husks, and yerba mate residues) introduced in a defined amount of 10 wt.%. The LPDE was selected as a potential matrix representing conventional petroleum-based polyolefins characterized by very low content and emission level of monoaromatic hydrocarbons and terpenes. In addition, an essential aspect of a novelty of preformed research is checking whether the defined addition of

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biocomposites to the polymer mass allows for a stable and repeatable emission profile of compounds that might be released from the introduced additives.

2. Materials and methods

2.1.Materials for candidates of LRM

Recycled low-density polyethylene (LDPE), obtained from the local recycling company (Katowice, Poland), was applied as a matrix to prepare investigated composites. It was characterized by a density of 0.9142 g·cm^{-3} and melt flow rate (MFR) of 1.35 g·10 min^{-1} (190 °C, 2.16 kg). Apple pomace (AP) was generated during the production of homemade apple juice from White Transparent apples using SilverCrest® SSJ 300 B2 Slow Juicer from Lidl (Germany). Sunflower husks (SH) were obtained during the pressing of sunflower oil using PS-101 screw oil press from P.U-H OLA (Poland). Yerba mate residues (YM) were generated during the brewing of Compuesta Hierbas from Amanda (Argentina) acquired from the online store *coffeedesk.pl* (Poland). This type contains 95% yerba mate produced with stems, anti-acid and digestive herbs – peppermint, pennyroyal, incayuyo, linden, boldo, mint, and lemon vervain. Mentioned type of wastes have been chosen as exemplary materials from different branches of food industry – juice production, oil production and beverages. They are characterized by different composition and it was supposed that their emission profile considering monoaromatic hydrocarbons and terpenes would differ, so they could be applied for detecting and assessing the emissions of different chemicals.

2.2.Preparation of polymer-based candidates for laboratory reference material

The samples were prepared by mixing in a molten state using a two-roll mill from Shaw Robinson (London, UK) at a temperature of 95°C. Samples were prepared in the air atmosphere. Its composition was not analyzed, but according to literature data it contains 78.084% of nitrogen, 20.946% of oxygen, 0.934% of argon, 0.041% of carbon dioxide, and 0.00268% of other gases including neon, helium, methane, hydrogen and krypton. Time of processing equaled 15 min, including the 3 min phase of polyethylene plastification and 12 min of melt blending of polymer matrix with 10 wt.% of selected filler. The resulting composites were then compression molded at 150°C and 4.9 MPa for 2 min and then kept under pressure at room temperature for another 5 min to solidify the material. Then, samples were vacuum-packed using SilverCrest® Kitchen Tools SV 125 C3 Vacuum Packer from Lidl (Germany) to reduce VOCs emissions during storage before analyses. The general view of investigated candidates for laboratory reference material (LRM) prepared based on low-density polyethylene (LDPE),

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and plant-based wastes are shown in Figure 1. The outer diameter of a single pellet/disc was 24.6 mm and the thickness was 1.1 mm (9.86 cm^2).

2.3.Characteristic of candidates for laboratory reference material

The chemical structures of prepared polyethylene-based materials were determined using Fourier transform infrared spectroscopy (FT-IR) analysis performed by a Nicolet Spectrometer IR200 from Thermo Fisher Scientific (Waltham, MA, USA). The device had an ATR attachment with a diamond crystal. Measurements were performed with 1 cm^{-1} resolution in the range from 4000 to 400 cm^{-1} and 64 scans. Provided FTIR spectra were averaged from at least 10 different spectra.

To measure the crystallization and melting temperatures, and determine the temperature window for the use of prepared materials, differential scanning calorimetry (DSC), was applied. The 5.0 ± 0.1 mg samples were placed in aluminum crucibles with pierced lids. They were heated from 20 to 200°C with a heating rate of 10°C·min^{-1} and then cooled back to the initial temperature at a cooling rate of 10°C·min^{-1}. The heating/cooling cycle was performed twice to erase the polymers' thermal history during the first heating. The measurements were conducted using a Netzsch 204F1 Phoenix apparatus (Netzsch, Selb, Germany) in an inert nitrogen atmosphere. From the DSC results, the crystallinity degree (X_{CR}) of the samples was calculated using formula (1) [17, 18]:

$$X_{CR} = \frac{\Delta H_m}{(1-\theta)\cdot\Delta H_{m100\%}} \cdot 100\% \tag{1}$$

where: ΔH_m – melting enthalpy of a sample, $\Delta H_{m100\%}$ – melting enthalpy of 100 % crystalline polyethylene, $\Delta H_{m100\%}$ = 293.6 J/g, θ – filler weight fraction.

2.4. Reagents and analytical equipment

The following solvents and reference solutions were used during the whole analytical procedure: (i) methanol for GC (MS SupraSolv®, Merck KGaA, Darmstadt, Germany) - solvent applied to prepare the appropriate calibration solutions; (ii) reference standard solution containing 20 terpenes dissolved in MeOH at content level 2000 µg·mL^{-1} of each (Cannabis Terpene Mix A certified reference material, TraceCERT®, Merck KGaA, Darmstadt, Germany) - external standard (ESTD) for calibration of the thermal desorption–gas chromatography–flame ionization detector (TD-GC-FID) system; (iii) reference standard solution containing

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deuterated toluene in MeOH at content level of 2000 μg·mL^{-1} (Toluene-d_8 solution certified reference material, TraceCERT®, Merck KGaA, Darmstadt, Germany) - internal standard (ISTD) for the assessment of the emission of total volatile organic compounds as well as an injection and organic compounds recovery standard.

To collect the organic compounds (including terpenes) emitted to the gaseous phase from investigated materials, the stainless steel tubes filled with Tenax TA sorption medium (60/80 mesh, stainless steel TD tube, O.D. × L 1/4 in. × 3 1/2 in., preconditioned, Merck KGaA, Darmstadt, Germany) were applied. Before employment, each Tenax TA tube was conditioned at elevated temperature (300°C for 30 min) under a stream of nitrogen (flow rate approx. 50 mL·min^{-1}; RH = 0%).

To perform the organic compounds emission studies from investigated materials, the stationary emission chambers system was used (Micro-Chamber/Thermal Extractor™ (μ-CTE™ 250, Markes International, Inc.). The mentioned device contains four equivalent (114 cm^3 capacity) cylindrical chambers made of high-quality polished steel. The studies using μ-CTE™ 250 might be performed in a dynamic (constant flow rate) or static mode, with a temperature range of 25°C to 250°C and an inert gas flow rate (dynamic mode) of 10 to 500 mL·min^{-1}. Detailed description, operating parameters, and potential application range of the Micro-Chamber/Thermal Extractor™ might be found elsewhere [14, 19-21].

To extract the organic compounds collected on a sorption medium (Tenax TA) the two-stage thermal desorption technique was used. To perform the effective extraction process, the stationary thermal desorption (TD) units were employed: (i) Markes Series 2 Thermal Desorption Systems; UNITY/TD-100 (Markes International, Inc.) combined with gas chromatography-flame ionization detector (GC-FID) system; (ii) Markes Unity v.2, (Markes International, Inc.) connected with GC combined with mass spectrometer (GC-MS) system. Both TD systems were equipped with multibed glass microtrap, cooled down to 0°C dedicated for determining organic compounds, including terpenes and the transfer line connecting TD units with appropriate GC systems was constantly heated up to 160°C. The separation, initial identification and quantitative determination of emitted organic compounds from investigated synthetic materials were carried out applying GC-FID system (Agilent Technologies 7820A GC System, FID working temperature – 280°C) equipped with GC capillary column (30 m × 320 μm × 5 μm, J&W DB-1, USA). The helium (He, 5.0) constant flow rate was 2.0 mL·min^{-1}. Moreover, to obtain a better identification of the emitted chemical compounds from the investigated materials the GC-MS system (GC Agilent Technologies 6890; 5873 Network Mass Selective Detector, Agilent Technologies) with the GC capillary column (30 m × 250 μm × 1

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μm, J&W HP-1MS, USA) was employed. The helium flow rate (He. 5.0) was 1.0 mL·min^{-1}. The MS ion source, the quadrupole mass analyser and GC-MS transfer line temperatures were 250°C, 150°C and 280°C, respectively. The identification of emitted chemical compounds was carried out employing the mass spectra database (NIST 2.0 Mass Spectral Library) attached to the MS system software (The NIST Mass Spectral Search Program for the NIST/EPA/NIH Mass Spectral Library Version 2.0d, USA).

2.5.General description of the applied analytical procedure

Before performing the analysis of prepared synthetic materials, the μ-CTE™ emission chambers were bake-out (conditioned) at elevated temperature (150°C) for 30 min under the continuous nitrogen gas flow rate (35 mL·min^{-1}; RH = 0%). Next background signal by investigation the blank samples – the chemical compounds emitted from empty emission chambers. After this, the general analytical procedure was introduced to assess the emissions of chemical compounds from prepared candidates for laboratory reference materials. Detailed information about the conditions and parameters of the applied analytical protocol was presented in the Figure 2. Regarding samples analyzed by the GC-MS system, one disc was selected and placed inside an emission chamber to identify emitted organic compounds from each pack of prepared synthetic materials. In this case the seasoning/conditioning parameters were as follows: seasoning temperature – 45°C; seasoning time - 30 min, seasoning mode – static mode; chemical compounds flushing/sampling time – 10 min; inert gas (RH = 0%) flow rate during sampling stage – 35 mL·min^{-1}.

To calculate the numerical values of linear retention index (LRI) of determined organic compounds, the mixture in acetone containing 1 μL of each chemical compound from C8 to C17 was prepared. The mentioned mixture was analyzed under the same thermal desorption and chromatographic conditions as real samples. Following obtained retention times, resulting from the chemical compounds present in investigated samples and the mixture of n-alkanes (C8 – C17), the numerical values of LRI were calculated according to the equation (2):

$$RI = 100n + \left(100 \times [TR_{(x)} - TR_{(n)}] \middle/ [TR_{(n+1)} - TR_{(n)}]\right) \quad (2)$$

In the above equation (2) TR is the determined retention time and (*n + 1*) and *n* are defined as the numbers of carbon atoms in the alkanes containing the prepared mixture which reached the detector after and before the unknown component of investigated sample *x*, respectively [22].

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As for the estimation of the values of TVOCs parameter (total volatile organic compounds), in line with literature information, the TVOC parameter is defined as the sum of all organic compounds, eluting between n-hexane and n-hexadecane (defined as analytical window) on non-polar/slightly polar stationary phases of the GC capillary column using flame ionization detector and quantifying as toluene equivalents [23-25].

2.6. Quality assurance and quality control

The mass (in nanograms) of determined organic compounds emitted from the investigated candidates for laboratory reference material and adsorbed on the applied sorption medium was calculated based on the external standard calibration method (ESTD). To perform the calibration of the TD-GC-FID system, a reference standard solution containing 2000 $\mu g \cdot mL^{-1}$ of each 20 terpenes (beta-Pinene; Camphene; alpha-Pinene; 3-Carene; alpha-Terpinene; (R)-(+)-Limonene; gamma-Terpinene L-(-)-Fenchone; Fenchol; (1R)-(+)-Camphor; Isoborneol; Menthol; Citronellol; (+)-Pulegone; Geranyl acetate; alpha-Cedrene; alpha-Humulene; Nerolidol; (+)-Cedrol; (-)-alpha Bisabolol) in MeOH and certificate standard solution of deuterated toluene in MeOH (2000 $\mu g \cdot mL^{-1}$) were used. Determination of the correlation between the mass of the analyte retained on the sorption bed on the detector signal of the applied TD-GC-FID system was performed based on previously published calibration procedure [14, 26-28].

Due to the fact, that the emitted organic compounds were at a low concentration level, only one range of calibration curves was needed. The mass ranges of prepared calibration curves were from 2 ng to 200 ng per sorption bed. Five calibration reference solutions (for five-point calibration curve) in 1 mL of MeOH were prepared. Each point on the calibration curve was repeated three times. The reference solution samples were analyzed under the same TD-GC-FID system conditions as the investigated synthetic materials. The correlation coefficients (R^2) of the calibration curves ranged from 0.992 to 0.998. To ensure the quality of the analytical procedure and results (QA/QC protocol), a randomly selected tube was again desorbed after each analysis. Before each analysis of prepared candidates for laboratory reference material, the value of a blank sample was investigated. Based on these studies it was possible to correct the obtained research results considering the purity of the applied gases, the wall-memory effects of applied seasoning and sampling devices, and the potential impurities that might occur in the chromatographic system. The analysis of blank samples was carried out applying analogous conditions as those used to analyze the real samples and the amount of the emitted organic compounds was corrected for the blank sample value [14, 26-28].

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Furthermore, to study the recovery of the thermal desorption process, a 1000 ng of deuterated toluene was introduced on a clean sorption medium (representative of a chemical compound that might be adsorbed most tangibly). Based on obtained results it was noticed that the recovery of determined organic compounds was in an acceptable level of approx. ± 5%. The instrumental (detector) limit of detection (ILD) value was calculated based on the signal-to-noise ratio (S/N) for samples with the lowest amount of deuterated toluene as well as selected organic compounds and reached an average value of 0.30 ng. The instrumental limit of quantitation (ILQ) was estimated as three times the ILD values.

3. Results and Discussion

3.1.FT-IR analysis

Figure 3 presents the FT-IR spectra of applied plant-based wastes. It can be seen that all of the materials show spectra typical for lignocellulose materials [29]. The broad peak at 3280-3350 cm^{-1} points to the stretching vibrations of hydroxyl groups, widely present in the structure of plant-based materials, including celluloses, lignin, and various polysaccharides [30]. Signals in the range of 2850-2930 cm^{-1} can be associated with the symmetric and asymmetric stretching vibrations of C-H bonds, which are present in the macromolecules of celluloses and lignin, main components of plant-based wastes, as well as the backbone of other components like lipids or proteins [31]. In the case of SH material, the enhanced intensity of these signals, and the presence of a minor signal at 3010 cm^{-1} indicate the presence of oils containing unsaturated fatty acids [32]. Around 1730 cm^{-1} were noted peaks attributed to stretching vibrations of carbonyl C=O bonds, while around 1640 cm^{-1} peaks of characteristic for the stretching vibrations of unconjugated C=O and C=C bonds in polysaccharides and lipids, which were most pronounced for SH filler, confirming the presence of oils [33]. Potent signals in the range of 990-1150 cm^{-1} were associated with the vibrations of δ bonds between carbon and oxygen atoms (in ester and ether groups), related to the chemical structure of analyzed materials [34].

Figure 4 shows FT-IR spectra obtained during spectroscopic analysis of LDPE-based candidates for laboratory reference material, typical for polyethylene materials [35]. Sharp peaks related to the stretching, bending and rocking C-H vibrations around 2914, 2840, 1464, and 730 cm^{-1} dominate in spectra due to the chemical structure of the LDPE backbone [36]. Except for them, spectra of composites containing apple pomace and yerba mate residues include only minor peaks in the range of 1090-1370 cm^{-1} characteristic for lignocellulose materials [37]. On the other hand, material filled with sunflower husk showed higher intensity

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of these peaks and the presence of an additional peak at 1744 cm^{-1}, which points to the migration of oils from the filler onto the composite surface during its processing [38]. Presence of this peak is in line with the structure of SH filler reported in Figure 3. Nevertheless, presented FT-IR spectra point to the efficient encapsulation of filler particles by LDPE macromolecules, which may be crucial for the long-term stability of organic compounds emissions from composites. Moreover, lack of peaks characteristic for carbonyl bonds in the FTIR spectra of prepared LDPE-based composites indicate that matrix was not degraded during processing [39, 40].

Figure 5 shows the thermograms obtained during DSC analysis of prepared composite materials and mean values of selected thermal parameters (melting Tm, crystallization Tc temperatures and crystallinity Xc). Peaks observed on the heating curves at 114.4-116.6°C are typical for low-density polyethylene grade [41]. It can be seen that there are no other peaks were noted, which points to the relatively high purity of the recycled matrix. Differences in melting temperatures between samples are associated with the changes in crystallite size. Lower values indicate the reduced size of crystallites, which may be related to the restrictions in spherulite growth caused by the presence of solid particles [42].

Despite the low susceptibility of polyethylene to the phenomena of heterogeneous nucleation, in the case under consideration, a different fillers' efficiency on the crystallinity level was observed, in a range that cannot be considered negligible. Moreover, the crystallization temperature, determined as the temperature position of the peak on the cooling curve, is the highest for material containing yerba mate residues, followed by apple pomace composite. Such an effect points to the presence of solid impurities, which may act as nucleating agents, increasing the crystallization rate [43]. Except for the main crystallization peak, a small exothermic peak was observed around 60°C. This effect is related to separate second crystallization of crystallites with various thicknesses, which is characteristic of polyethylene grades with long-chain branches in their structure, as previously noted for LDPE [44]. Nevertheless, it does not affect the possibility of using applied material as the matrix for laboratory reference material. Concluding, the results of DSC measurements indicate that the prepared materials could be efficiently applied as laboratory reference materials even at elevated temperatures around 100°C. However, as heating curves indicate, the melting of LDPE occurs over a wide range of temperatures. Therefore, the changes in LDPE crystalline structure could affect the emission profile and emission rate at various temperatures of organic compounds.

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3.2. Linear retention index of determined representatives of organic compounds

The results of calculated values of LRI for chemical compounds emitted and identified from the investigated samples of candidates for LRM are listed in Table 1. From 20 chemical compounds enclosed in the reference standard solution (Cannabis Terpene Mix A), 15 were identified in the studied materials. The highest number of compounds classified as terpenes was identified in the samples of materials with the addition of yerba mate residues (15 compounds), and the smallest - with the addition of sunflower husks (two terpenes and one representative of monoaromatic hydrocarbons). The ranges of calculated values of LRI for determined chemical compounds correspond to the ranges of LRI published in scientific literature determined using similar chromatographic conditions. Several deviations might be caused by the combination of random as well as systematic errors. At this point it should be highlighted that during described studies, the sample injection process was performed using thermal desorption techniques connected directly to the GC column. In the literature data, the injection was performed mainly in a traditional way using a GC injector. Moreover, the presence of variations in calculated LRI values might be the consequence of the use of GC columns characterized by different parameters, such as internal diameter, film thickness, as well as service life. Mentioned factors might slightly affect the analytes retention times, pick shape and the chromatogram resolution. Nevertheless, the presence of listed in Table 1 chemical compounds was confirmed (above 85% compatibility) by analyzing the investigated samples using the MS detector.

3.3. The emission rate of determined chemical compounds from investigated candidates for LRM

3.3.1. Dependence between the emission rate of the determined organic compounds and LRM seasoning/conditioning time

Considering the obtained results, the relationship between the emission rate of identified and determined organic compounds and seasoning/conditioning time was investigated. In Figure 6 and Figure 7, the relationship between the emission rate of TVOCs and the sum of terpenes (calculated based on the identified and determined organic compounds released to the gaseous phase from investigated candidates for LRM) and different seasoning/conditioning periods was shown. Detailed information about the correlation between terpenes' emissions and seasoning/conditioning time for studied polymeric materials was shown in Supplementary Figures from 1 to 3. The error bars shown in Figure 6 and Figure 7 represent the standard deviation values for the performed measurements (n = 3).

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In the case of candidates for LRM with the addition of YM and AP (Figure 6), a clear relationship was observed between the samples seasoning/conditioning time in the chamber and the total amount of VOCs released into the gaseous phase, including identified and determined representatives of terpenes. Moreover, improving the interpretation of these data with the analysis of the information presented in Supplementary Figure 1 (SF1) and Supplementary Figure 2 (SF2), it can be observed that in the case of material with the addition of YM, almost all of the identified and determined organic compounds were characterized by a strong correlation between the emission rate and the seasoning/conditioning time. In the case of materials with the addition of AP, the organic compounds whose emission rate was dependent on the seasoning/conditioning time constituted the majority but not as numerous as in the case of the materials with the addition of YM. On the other hand, the candidates for LRM with the addition of SH (Figure 7) essentially did not show any correlation between the emission rate of identified and determined organic compounds and the seasoning/conditioning time. This proves the lack of factors/additives that might be considered as the emission source of terpenes (dried fruit or citrus pomaces and residues) or aromatic hydrocarbons (residues of solvents or dyes).

Calculating the numerical values of the PCC (Pearson's correlation coefficient) in the case of the results obtained for the samples of materials with the addition of YM for the determined total parameters – TVOCs and sum of terpenes, it was found that these values were respectively -0.666 and -0.676. This confirms the existence of a strong inverse relationship (ranging from -0.60 to -0.80) [48, 49] between the investigated total parameters and seasoning/conditioning time. In the case of materials with the addition of AP, the numerical values of the PCC for determined total parameters were -0.769 and -0.712, respectively. It also proves the existence of a strong inverse relationship between the emission rates of identified and determined organic compounds and the seasoning/conditioning time of the candidates for LRM inside an emission chamber. On the other hand, when referring to the research conducted on material with SH addition, a very weak relationship between the seasoning/conditioning time and the determined total parameters, as well as in a case of identified and determined individual organic compounds was observed. Moreover, as can be observed in Figure 7, the amount of emission rate of the determined terpenes representatives, and the total amount of VOCs were much lower than in the case of the other investigated candidates for LRM. Estimated values of PCC confirm the presence of a weak correlation (0.330 and -0.122) between seasoning/conditioning time and the emission rate of assessed total parameters. This proves that in the case of materials with the addition of SH, both the emission rate of TVOCs and determined terpenes are not directly dependent on the seasoning/conditioning time of the sample. Additionally, it can be concluded

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that the material filled with 10% of SH is a low-emission material in terms of compounds from the group of aromatic hydrocarbons and terpenes, and the TVOC parameter might be mainly related to the emission rate of compounds from the group of aliphatic hydrocarbons resulting from the linear structure of the applied polymer matrix.

Regarding the results for the synthetic material with the addition of YM, there is a clear relationship between the emission profiles of the TVOCs and the total amount of identified and determined terpenes. This may be a consequence of the fact that the YM waste is a mixture of various organic ingredients (fruit and citrus waste), which may be the source of the emission of aromatic compounds including terpenes. Considering the percentage of identified and determined terpenes, it was found that, depending on the seasoning/conditioning time, it fluctuated in the range from 24.72% to 36.51% (the standard deviation for these results was low - 3.29%). However, in the case of a candidate for LRM with the addition of AP, similar characteristics of the emission profile for TVOC and the sum of determined terpenes were observed. Nevertheless, it is not as uniform as for the polymer materials with the addition of YM wastes. It may be mainly due to the use of only one type of additive (not a mixture of bioadditives), which are pomace from one type of fruit - apples. The percentage emission rate of terpenes in the total emission rate of VOCs ranged from 5.90 to 20.10% with a standard deviation of 4.20%. Furthermore, considering the information enclosed in Supplementary Materials (Supplementary Figures 1-3) regarding the emission profile of individual compounds from the terpenes group, as well as toluene and furfural, it can be noticed that in most cases there is a similar relationship in the aspect of seasoning/conditioning time as for the previously mentioned total parameters.

In order to better illustrate these relationships, Table 2 presents information on the calculated curves parameters ($y = ax + b$) determined as a $\log_{10}$ of the emission rate in relation to the seasoning/conditioning time, as well as the calculated numerical values of the PCC parameter. The use of the logarithmic scale allowed for better visualization of a potential linear relationship between the emission rate of a given compound and the seasoning/conditioning time of the tested material inside the chamber. In Table 2, compounds were highlighted for which both the numerical value of the coefficient of determination (R^2) and the PCC confirmed a strong or very strong relationship between the emission rate and the seasoning/conditioning time.

Referring to the data summarized in Table 2, in the case of samples with the addition of YM, the vast majority of emitted, identified and determined compounds were characterized by a strong or very strong relationship with the seasoning/conditioning time. A similar relationship was noted for investigated polymeric materials with AP addition. However, because it is one

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type of additive (YM was a mixture of stems, anti-acid and digestive herbs – peppermint, pennyroyal, incayuyo, linden, boldo, mint, and lemon vervain), a slightly smaller number of compounds was characterized by a strong or very strong dependence of emissions on the seasoning/conditioning time. However, for samples with the addition of SH, there were no clear relationships between the identified and determined compounds and the seasoning/conditioning time – as in the case of the calculated summary parameters (TVOCs and sum of terpenes). The lack of even medium relationship between the identified compounds and the time of samples seasoning/conditioning may indicate that the investigated polymeric material with the addition of SH emits mainly organic compounds other than terpenes or aromatic hydrocarbons. This is associated with the different chemical composition of SH filler compared to AP and YM (sunflower husks may not contain the determined compounds, or they might be present at a very low content level which is difficult to quantify by the applied techniques). According to information published by Lattuati-Derieux et al. [50], Pajaro-Castro et al. [51], Mitchell et al. [52], mainly aliphatic hydrocarbons such as n-dodecane, n-undecane, n-tridecane, n-tetradecane, n-hexadecane, n-pentadecane, n-heptadecane, as well as nonanal might be emitted to the gaseous phase from raw LDPE matrix. These compounds were identified during the GC-FID analysis in the case of determination of retention indexes (analysis of retention times of obtained signals for organic compounds present in the mixture of aliphatic hydrocarbons from C8 to C17) and GC-MS analysis (analysis of obtained spectra for individual compounds and degree of compliance with the NIST mass spectra library agreement above 90%), however they were not subject to quantitative analysis. In addition, such compounds are released into the gaseous phase only under the elevated temperature (above 65^{o}C), or after a sufficiently long time of seasoning/conditioning the polymeric material in the emission chamber.

Negative numerical values of the slope factor of the curve and the PCC parameter indicates an inverse relationship – the amount of emissions decreases with the passage of the seasoning/conditioning time. This is a common phenomenon noted in the literature for materials analyzed in the process of estimating long-term exposure in environmental test chambers [53, 54]. With the passage of the seasoning/conditioning time, the intensity of emissions of organic compounds to the gaseous phase is reduced, especially the more volatile ones, such as aromatic hydrocarbons or terpenes. However, after a certain time, this process slows down and the level of emissions is set at a relatively constant level, with slight fluctuations. In the case of discussed investigations, it was noted that after 4 hours from placing the testing material in the chamber, the emission level of the determined compounds reached a constant level. The occurrence of this phenomenon may be the basis for the conclusion that the developed materials with the

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addition of YM or AP can be considered as reference materials for emissions of determined compounds for long-term studies - calibration of small emission chambers, portable emission cells (field and laboratory emission cells – FLECs) [11, 55] or for performing comparative analyses between scientific centers. Furthermore the application of developed LRM might be considered as an alternative solution for modelling large-scale, time and labor consuming reference rooms – specially designed indoor areas in which several exposure scenarios are considered and wide spectrum of simulations are performed [56]. Due to the addition of AP to the polymer matrix, it can be considered the LRM for the furfural emission. Confirmation that this compound is emitted mainly from products containing the addition of apples are literature reports [54, 55] and confirmation of the presence of this compound during the GC-MS analysis (degree of compliance with the NIST mass spectra library database above 95%). The additional confirmation of this fact is the observation of emissions of significant amounts of its derivative with a degree of compliance above 91% - 5-Hydroxymethyl-2-furaldehyde (CAS. No. 67-47-0). Following the information listed in the literature, mentioned compounds (furfural and its derivative) are generated mainly during the long-term storage, drying or cooking of fruits such as apples [57, 58].

3.3.2. Dependence between the emission rate of the determined organic compounds and LRM seasoning/conditioning temperature

Another critical aspect in the field of emission rate studies considering synthetic materials is assessing the relationship between the seasoning/conditioning temperature and the amount of the analytes emitted into the gaseous phase. Several investigations performed in the scientific centers and published in the literature research results confirms that VOCs emissions from indoor materials is affected significantly by temperature [59-61]. The studies were conducted at temperatures ranging from room temperature to 60^{o}C at defined constant time (30 min). Performing the investigations at a higher temperature is "unreasonable" because, in real conditions (in an indoor environment), indoor materials are not heated above this value (even in the case of the application of a floor heating system). In Figure 8 and Figure 9, the relationship between the emission rate of summary parameters (TVOCs and sum of identified and determined terpenes) calculated for investigated candidates for LRM and different seasoning/conditioning temperature conditions was illustrated. Detailed information about the relationship between the emission rate of representatives' aromatic hydrocarbons and terpenes and seasoning/conditioning temperature was shown as values of determination coefficients and

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PPCs in Table 3. The error bars enclosed in Figure 8 and Figure 9 represent the standard deviation values for the performed measurements (n = 3).

Analyzing the data in Figure 8, it might be observed that the existence of a clear relationship between the size (intensity) of the emission defined by the calculated summary parameters (TVOCs and sum of terpenes) and the seasoning/conditioning temperature of polymeric materials with bioadditives. Considering the values of the R^2 for materials with the addition of AP and YM (Figure 8) it might be noticed that there is a very strong relationship between temperature (from 21 to 60^{o}C) and the total amount of organic compounds and terpenes emitted into the gaseous phase. Confirmation of the presence of a very strong relationship between the calculated summary parameters and the temperature are estimated values of the PCC - for materials with the addition of AP they were 0.987 (TVOCs) and 0.954 (sum of terpenes), while for materials with the addition of YM they were 0.936 and 0.934, respectively. This indicates that the increase in the temperature of seasoning LRM samples with bioadditives (derived from citrus and fruit wastes) causes a significant increase in the total emission of the total amount of compounds classified as terpenes and aromatic hydrocarbons (on the example of toluene and furfural). For LDPE material with SH additives (Figure 9), they were 0.900 and 0.836, respectively. However, in this case, the total parameters for 21^{o}C were not determined, because at that time the room temperature was nearly 25^{o}C. In cases where the level of emissions of compounds was below ILD, in order to estimate the PCC parameter, a numerical value of ILD was used for further calculation.

Taking into account the information summarized in Table 3, it can be noted that over half of the determined terpenes emitted from LDPE materials with the addition of AP and YM showed strong or very strong (R^2 and PCC values above 0.60) dependence on temperature. This type of dependence proves that the objects being the subject of the research are the sources of the emission of the determined chemical compounds. In addition, as shown in Table 3, a sample of LDPE material with AP addition was a clear source of furfural emission, very strongly dependent (PCC and R^2 above 0.80) on temperature. This is mainly because the addition of only one type of material - apple pomace - was used as the filler.

In the case of LDPE material with the addition of YM, which consists of a mixture of stems, peppermint, pennyroyal, incayuyo, linden, boldo, mint, and lemon vervain, there was no strong or very strong relationship between the seasoning/conditioning temperature and the intensity of emission of furfural or toluene. On the other hand, a very strong relationship (above 0.80) was noted for identified and determined terpenes from α-Pinene to (1R)-(+)-Camphor. As in the previously described case (in 3.3.1 sub-chapter) of the dependence of chemical compound

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emissions on the seasoning/conditioning time, the LDPE material with the addition of SH did not show a statistically significant correlation between the emission rate and the seasoning/conditioning temperature. The polymer matrix, which was LDPE, is mainly a source of emissions of aliphatic hydrocarbons, which are released into the gaseous phase from such materials at higher temperatures than the maximum temperature of the performed studies (above 65°C). One of the potential causes of this phenomenon that can be taken into account is the fact that presence of SH in the polymer matrix structure might limit the emission of determined chemical compounds to the gaseous phase, due to its potential sorption abilities. According to the research performed by Saleh et al. [62] the specific surface area of sorption materials prepared based on the sunflower husks oscillates from 1.782 to 3.850 $m^2 \cdot g^{-1}$ (based on the research performed using the Brunauer–Emmett–Teller specific surface area analysis). For this reason, this kind of biological material was used, e.g. as a biosorbent for removing cationic dyes and various heavy metals, as well as for wastewater decontamination [62]. Nevertheless, confirmation of the occurrence of this type of phenomenon (reduction of the emission of organic compounds as a result of the sorption abilities of SH) in the aspect of described candidates on the LRM requires further, more advanced research.

4. Conclusions and future directions

In a described pilot interdisciplinary research the non-commercial laboratory-made candidates for laboratory reference materials were prepared based on the synthetic polymeric matrix into which biocomposites constituting waste from industrial plant processing were introduced. Taking into account obtained results, it might be concluded that designed and developed materials consisting of LDPE matrix and 10% wt. of bioadditives – yerba mate residues and apple pomace might be successfully considered as a candidate for LRM in the case of selected terpenes (especially compounds from 136.23 up to 154.25 of molecular weight) emissions investigation. Additionally, prepared polymeric materials with the apple pomace addition might be introduced in the preliminary studies as an emission laboratory material for furfural. Analyzing the preliminary results, it might be stated that developed materials will allow for an optimal comparison of self-designed and home-made emission chambers and commercially available analytical devices, such as small-scale stationary emission test chambers, field and laboratory emission cells, or in the future perspective home-made passive flux samplers.

For samples of materials made of LDPE and with the addition of SH, no clear and statistically significant relationships were found between the emission of the determined compounds and the seasoning/conditioning temperature or time. It was mainly caused by the possibility of

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sorption of chemical compounds classified as VOCs by SHs (relatively well-developed specific surface of this material), as well as presence of oils containing unsaturated fatty acids. Nevertheless, the lack of a desired positive result in this aspect opened the door to another research trend related to the ability to reduce the emission of pollutants to the gaseous phase (indoor environment) by plastic materials by adding an appropriate amount of filler in the form of SHs. Due to the possibility of losses in the content of the determined chemical compounds, prepared polymeric material was preserved by vacuum wrapping it in a PE hermetic package. It is recommended that the material should be stored at reduced temperature (e.g in the refrigerator, temperature range 2 – 8) and in airtight or original packaging, to further reduce potential VOCs emissions before analyses. Emissions of aromatic hydrocarbons and terpenes will be investigated every 6 months to verify the long-term stability of the developed LRM and to confirm the choice of packaging and storage conditions used for the selected polymeric material.

Performed pilot research and obtained preliminary results create promising database containing information about the structure, material characteristics, and emission parameters of designed candidates for LRM. Additionally, the emission of individual compounds effects from their natural occurrence in the bioadditives introduced to the polymer material. It is a "greener" and environmentally friendly solution in relation to the described in the literature solutions in which appropriate chemical reagents are used. This aspect might be considered a beneficial small-scale side effect - the possibility of managing and using residues from industrial plant processing. Another valuable aspect is that prepared candidates for LRM might be applied directly into almost every small-scale analytical device used as the emission chamber (dynamic or static gaseous phase analysis) to evaluate its performance.

It is necessary to ensure the quality control of inter-laboratory studies related to the determination of VOCs emitted from samples that very often have a complex matrix composition. The ability to adequately compare laboratories that analyze VOCs requires the availability of standards and reference materials with low uncertainty levels. Primary and secondary standards are necessary for accurate data correlation, which is a prerequisite for adequate regulation of toxic organic pollutants [63]. On the other hand, reference materials play an essential role in all elements of the quality assurance system for measurement results. Quality control is based on the analysis of reference materials using the analytical method under test and comparing the results obtained with the reference values. Therefore, it is important to continuously enrich the range of available reference materials, so that they are as "identical" as

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possible in chemical matrix composition and physical form to the samples tested, and that the substance determined is as close as possible to its content in the samples tested.

In Europe, the Construction Products Regulation (CPR, 2011/305/EU) is in force, setting out basic requirements for the design and construction of construction works where emissions of toxic gases, volatile organic compounds (VOCs), particles are emissions, etc. from building materials are concerned. At the same time, an increasing number of professional commercial and non-commercial laboratories are being established to perform emission tests to evaluate products intended for indoor use. It is, therefore, necessary to ensure the comparability of test results so that the proficiency of a laboratory can be proven. Participation in inter-laboratory tests is a means of demonstrating a laboratory's proficiency. At present, the main problem for such comparisons is the lack of reference materials with known emission factors for the target substances. Due to the wide variety of VOCs typically emitted from building materials, furniture and other products used indoors, there is still a lack of suitable reference materials covering a broader spectrum of compounds. Therefore, there is a strong need to develop new types of suitable reference materials as tools for obtaining reliable analytical information.

Considering positive aspect of obtained pilot research it might be conclude that prospective LRM for terpenes and furfural emissions with low-emitting LDPE matrix was developed. Continuing this field of research, the future studies will be expand to implement to low-emitting polymer matrix (LDPE or HDPE) another bioadditives such as citrus residues comes from mandarin, or cocoa husk as well as dried coffee grounds. These types of materials allow for the management (even if the recycling scale of the project is not too broad) of waste from the processing or thermal treatment of natural products. In addition, the implementation of specific types of bioadditives into the polymer matrix in the appropriate weight ratio can create a precedent for the development of new type of reference material candidates focused on the controlled and known emission rate of specific chemical compounds of natural origin.

5. Acknowledgements

Authors would like to express their gratitude to Krzysztof Klewicz for his contribution in laboratory studies performing part of a research and for gathering and elaborating an appropriate database.

6. Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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8. Figure captions

Figure 1. General view of an investigated candidates for laboratory reference material (LRM) prepared based on low-density polyethylene (LDPE) and plant-based wastes: A – LDPE with sunflower husks; B – LDPE with yerba mate residues; C – LDPE with apple pomace.

Figure 2. A general information about the analytical protocol employed for the determination of investigated representatives of monoaromatic hydrocarbons and terpenes emitted from candidates for laboratory reference material**.**

Figure 3. The results of FT-IR analysis of introduced plant-based wastes

Figure 4. The results of FT-IR analysis of LDPE-based candidates for laboratory reference material.

Figure 5. The general view of thermograms obtained during DSC analysis of prepared composite materials.

Figure 6. Relationship between seasoning/conditioning time of investigated candidates for LRM with yerba mate residues (A) and apple pomace (B) addition and the estimated specific emission rate of total VOCs as well as the sum of identified and determined terpenes.

Figure 7. Relationship between seasoning/conditioning time of investigated candidate for LRM with sunflower husks (SH) addition and the estimated specific emission rate of total VOCs as well as the sum of identified and determined terpenes.

Figure 8. The relationship between the seasoning/conditioning temperature of investigated candidates for LRM with yerba mate residues (A) and apple pomace (B) addition and the emission rate of total VOCs as well as the sum of identified and determined terpenes.

Figure 9. The relationship between the seasoning/conditioning temperature of investigated candidates for LRM with sunflower husks (SH) addition and the emission rate of total VOCs as well as the sum of identified and determined terpenes.

9. List of Supplementary Materials

Supplementary Figure 1. Relationship between seasoning/conditioning time of investigated candidate for LRM with YM addition and the estimated specific emission rate of toluene, furfural and identified and determined terpenes.

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Supplementary Figure 2. Relationship between seasoning/conditioning time of investigated candidate for LRM with AP addition and the estimated specific emission rate of toluene, furfural and identified and determined terpenes

Supplementary Figure 3. Relationship between seasoning/conditioning time of investigated candidate for LRM with SH addition and the estimated specific emission rate of toluene, furfural and identified and determined terpenes

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Table 1. Calculated retention indices of representatives of monoaromatic hydrocarbons and terpenes emitted to gaseous phase from investigated candidates for LRM.

Chemical compound	CAS No.	Molecular weight	Range of LRI on DB-1 for investigated samples based on GC-FID analysis	Type of a sample in which the compound was identified	Range of LRI based on literature data on similar GC column[(a)]
Toluene	108-88-3	92.14	765-769	AP, SH, YM	762-770 [46]
Furfural	98-01-1	96.08	805-810	AP, YM	828-832 [47]
α-Pinene	80-56-8	136.23	933-936	AP, YM	930–938
Camphene	79-92-5	136.23	953-956	YM	941–953
β-Pinene	127-91-3	136.23	978-982	AP, YM	968–978
3-Carene	13466-78-9	136.23	1011-1015	YM	1001–1010
(R)-(+)-Limonene	5989-27-5	136.23	1030-1035	AP, YM	1020–1027
L-(-)-Fenchone	7787-20-4	152.23	1098-1105	AP, YM	1059–1087
Fenchol	2217-02-9	154.25	1113-1118	AP, YM	1088–1122
(1R)-(+)-Camphor	464-49-3	152.23	1120-1127	YM	1118–1130
(+/-)-B-Citronellol	106-22-9	156.27	1212-1218	YM	1208–1215
(R)-(+)-Pulegone	89-82-7	152.23	1223-1230	AP, YM	1215–1230
(−)-α-Cedrene	469-61-4	204.35	1410-1417	AP, SH, YM	1399–1416
α-Humulene	6753-98-6	204.35	1449-1454	AP. YM	1443–1455
Nerolidol	3790-78-1	222.37	1524-1530	AP, YM	1516–1533
(+)-Cedrol	77-53-2	222.37	1597-1602	AP, YM	1584–1609
(−)-α-Bisabolol	23089-26-1	222.37	1658-1668	AP, SH, YM	1663–1674

(a) Based on data published by Babushok et al. [45] – RI values of essential oil components for GC dimethylsilicone stationary phase

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Table 2. Calculated numerical values of curve parameters and Person's Correlation Coefficient (PCC) to estimate the relationship between the specific emission rate (ng per gram of sample per hour) of detected organic compounds and the seasoning/conditioning time (in hours) of investigated materials.

Numerical values of curve parameters y = AX + B				
Samples of candidate for LRM with YM addition				
Emitted compound	**A**	**B**	**R^2**	**PCC***
Toluene	-0.162	1.315	**0.765**	**-0.647**
Furfural	-0.201	1.172	**0.799**	**-0.673**
α-Pinene	-0.207	1.557	**0.849**	**-0.702**
Camphene	-0.144	0.994	**0.885**	**-0.724**
β-Pinene	-0.167	1.594	**0.807**	**-0.669**
3-Carene	-0.181	0.904	0.712	-0.529
(R)-(+)-Limonene	-0.144	1.360	**0.814**	**-0.691**
L-(-)-Fenchone	-0.169	1.575	**0.782**	**-0.667**
Fenchol	-0.176	1.802	**0.743**	**-0.653**
(1R)-(+)-Camphor	-0.167	1.157	**0.712**	**-0.609**
(R)-(+)-Pulegone	-0.186	1.435	**0.867**	**-0.700**
(−)-α-Cedrene	-0.186	1.112	**0.913**	**-0.719**
α-Humulene	-0.165	1.110	0.737	-0.585
Nerolidol	-0.187	1.386	**0.824**	**-0.708**
(+)-Cedrol	-0.185	1.203	**0.793**	**-0.735**
(−)-α-Bisabolol	-0.207	1.103	**0.835**	**-0.693**
Samples of candidate for LRM with AP addition				
Emitted compound	**A**	**B**	**R^2**	**PCC**
Furfural	-0.154	2.968	**0.886**	**-0.775**
α-Pinene	-0.133	1.574	**0.869**	**-0.773**
β-Pinene	-0.160	1.316	**0.768**	**-0.742**
(R)-(+)-Limonene	-0.063	1.040	0.159	-0.598
γ-Terpinene	-0.036	0.400	0.032	0.067
L-(-)-Fenchone	-0.167	1.251	**0.778**	**-0.775**
Fenchol	-0.159	1.580	**0.803**	**-0.749**
(1R)-(+)-Camphor	-0.149	1.061	**0.823**	**-0.811**
(+/-)-B-Citronellol	-0.110	0.652	**0.690**	**-0.814**
(R)-(+)-Pulegone	-0.090	0.969	0.203	-0.510
Alpha-Cedrene	-0.167	1.141	**0.726**	**-0.685**
Alpha-Humulene	-0.175	0.935	**0.856**	**-0.695**
Nerolidol	-0.170	1.391	**0.795**	**-0.641**
(+)-Cedrol	-0.086	0.759	0.180	0.001
(−)-α-Bisabolol	-0.123	0.969	0.428	-0.610
Samples of candidate for LRM with SH addition				
Emitted compound	**A**	**B**	**R^2**	**PCC**
(−)-α-Cedrene	-0.0066	0.084	0.0044	-0.498
α-Humulene	0.0065	0.065	0.0014	0.063
Nerolidol	-0.0170	0.067	0.207	0.813
(+)-Cedrol	-0.0104	0.353	0.0032	0.205
(−)-α-Bisabolol	-0.0027	0.428	0.0002	-0.0047

y - logarithm (LOG) of emission rate of defined compound; X - seasoning/conditioning time of investigated material; PCC - Pearson's correlation coefficients at a significance level of p < 0.05

**Relationship criteria (based on Liang et al [48] and Yee et al [49]: 0.0 ÷ 0.2 – very weak (no or negligible); 0.2 ÷ 0.4 – weak; 0.4 ÷ 0.6 moderate; 0.6 ÷ 0.8 strong; above 0.8 - very strong (1.0 perfect relationship).*

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Table 3. Calculated numerical values of curve parameters and Person's Correlation Coefficient (PCC) to estimate the relationship between the emission rate (ng per gram of sample) of detected organic compounds and the seasoning/conditioning temperature (in °C) of investigated materials.

Numerical values of curve parameters $y = AX + B$				
Samples of candidate for LRM with YM addition				
Emitted compound	**A**	**B**	**R^2**	**PCC****
Toluene	0.247	6.121	0.305	0.553
Furfural	0.075	6.192	0.247	0.497
α-Pinene	0.237	8.950	**0.639**	**0.799**
Camphene	0.432	-9.003	**0.930**	**0.964**
β-Pinene	1.311	-22.749	**0.951**	**0.975**
3-Carene	0.167	-0.452	**0.559**	**0.748**
(R)-(+)-Limonene	2.676	-58.596	**0.802**	**0.896**
L-(-)-Fenchone	1.689	-38.016	**0.964**	**0.982**
Fenchol	2.148	-33.425	**0.911**	**0.955**
(1R)-(+)-Camphor	0.150	1.942	**0.830**	**0.911**
(R)-(+)-Pulegone	0.079	8.049	0.286	0.534
(−)-α-Cedrene	-0.445	36.484	0.315	-0.561
α-Humulene	-0.308	25.237	0.163	-0.403
Nerolidol	-0.030	12.603	0.030	-0.173
(+)-Cedrol	-0.038	7.443	0.112	-0.335
(−)-α-Bisabolol	-0.140	10.198	0.297	-0.545
Samples of candidate for LRM with AP addition				
Emitted compound	**A**	**B**	**R^2**	**PCC**
Furfural	29.825	-468,715	**0,985**	**0,992**
α-Pinene	0.653	2,786	**0,738**	**0,859**
β-Pinene	0.943	-14,885	**0,936**	**0,968**
(R)-(+)-Limonene	2.672	-66,945	**0,823**	**0,907**
γ-Terpinene	0.036	1.423	0.492	0.701
L-(-)-Fenchone	1.196	-26.400	**0.959**	**0.979**
Fenchol	2.583	-72.945	**0.921**	**0.960**
(1R)-(+)-Camphor	0.179	1.181	**0.723**	**0.850**
(+/-)-B-Citronellol	0.391	-10.516	**0.927**	**0.963**
(R)-(+)-Pulegone	-0.106	15.134	**0.623**	**-0.789**
Alpha-Cedrene	0.090	6.350	0.116	0.340
Alpha-Humulene	0.331	-1.661	**0.685**	**0.828**
Nerolidol	0.160	6.811	0.480	0.693
(+)-Cedrol	0.056	4.661	0.326	0.571
(−)-α-Bisabolol	1.375	32.502	0.059	0.243
Samples of candidate for LRM with SH addition				
Emitted compound	**A**	**B**	***R^2**	***PCC**
(−)-α-Cedrene	-2.192	41.36	0.329	-0.574
α-Humulene	-6.832	41.59	0.329	-0.574
Nerolidol	-0.498	41.27	0.329	-0.574
(+)-Cedrol	-1.085	41.30	0.329	-0.574
(−)-α-Bisabolol	-2.593	41.38	0.329	-0.574

y - emission rate of defined compound; X - seasoning/conditioning temperature of investigated material; PCC - Pearson's correlation coefficients at a significance level of $p < 0.05$
** identical values of PCC and R^2 parameters are caused by the fact that in significant cases (in temperature conditions below 45°C) measured compounds were below ILD and for the further calculations the calculated value of ILD was applied*
*** Relationship criteria (based on Liang et al [48] and Yee et al [49]): 0.0 ÷ 0.2 – very weak (no or negligible); 0.2 ÷ 0.4 – weak; 0.4 ÷ 0.6 moderate; 0.6 ÷ 0.8 strong; above 0.8 - very strong (1.0 perfect relationship).*

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PREPARATION OF CANDIDATES FOR LABORATORY REFERENCE MATERIAL TO EMISSIOS STUDIES

- Weighting and samples description;
- Placing the studied samples into the emission chambers system

SAMPLING THE CHEMICAL COMPOUNDS EMITTED TO THE GASEOUS PHASE FROMINVESTIGATED SYNTHETIC MATERIALS

- Seasoning/conditioning of investigated materials under static conditions, without forced flow rate of nitrogen gas through the chambers - the gas outlets from the chambers were sealed with a rubber septum;
- Seasoning/conditioning at predefined time intervals: 15 min; 30 min; 60 min; 90 min; 120 min; 240 min; 360 min; 480 min – starting from the moment when the studied samples were placed inside the chambers;
- Seasoning/conditioning at defined constant time (30 min) in different temperatures: 21°C; 25°C; 35°C; 45°C; 60°C;
- After the defined samples seasoning time, from each of chambers outlets the septum was removed and the stainless steel tube filled with Tenax TA was installed;
- At the end, the nitrogen gas flow rate was turn on and the chemical compounds present in gaseous phase inside a chamber were washed out and collected on the applied sorption medium – nitrogen flow rate 35 $mL \cdot min^{-1}$ for 5 min.

LIBERATION OF CHEMICAL COMPOUNDS RETAINED ON THE SORPTION MEDIUM

- *The 1st stage of thermal desorption process:*
  - Tenax TA tube temp. - 290°C;
  - microtrap temp. - 0°C;
  - desorption time – 15 min;
  - inert gas flow rate (helium) – 50 $mL \cdot min^{-1}$
- *The 2nd stage of thermal desorption process:*
  - microtrap desorption temperature - 300°C;
  - microtrap ballistic heating time – 5 min
  - inert gas flow rate (helium) passing through the microtrap directly to the GC column – 2.0 $mL \cdot min^{-1}$

SEPARATION, IDENTIFICATION AND FINAL DETERMINATION OF ANALYTES

- *Gas chromatography technique equipped with flame ionization detector (GC-FID)*; oven working program: initial temperature – 50°C maintained for 1 min, next increased 15°C$\cdot min^{-1}$ up to 120°C, and maintained for 2 min, after this increased with the rate 7°C$\cdot min^{-1}$ up to 260°C and held for 5 min.
- *Gas chromatography technique combined with mass spectrometer (GC-MS)*; oven working program: initial temperature – 50°C maintained for 1 min, next increased 15°C$\cdot min^{-1}$ up to 120°C, and maintained for 2 min, after this increased with the rate 7°C$\cdot min^{-1}$ up to 260°C and held for 5 min.

DATA ANALYSIS

- Identification and quantitative determination of emitted organic compounds based on reference solutions and obtained calibration curves;
- Screening identification of emitted organic compounds based on calculated linear retention indexes (LRI);
- Additional identification of emitted organic compounds based on GC-MS chemical compounds mass spectral library (NIST Mass Spectral Library)

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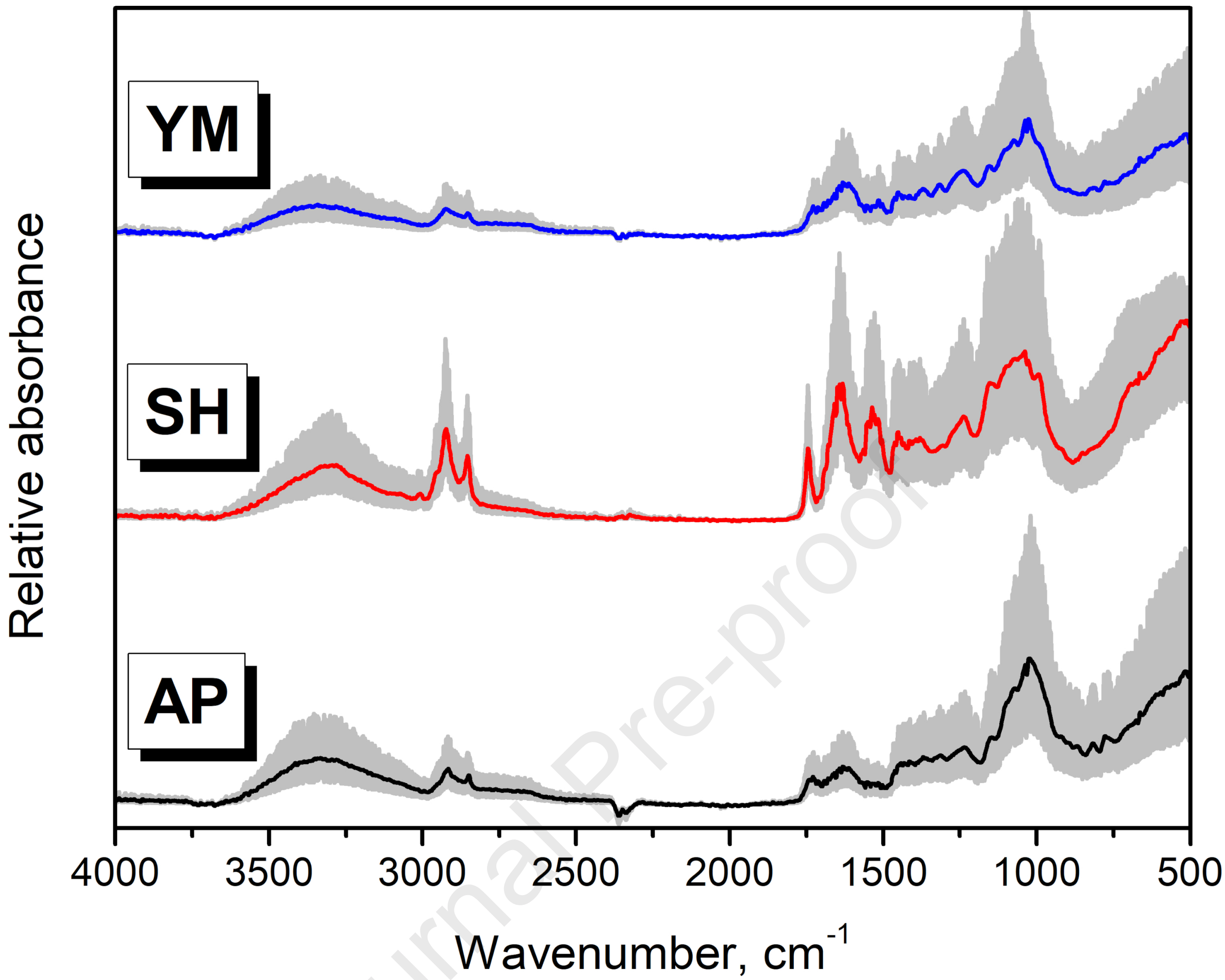

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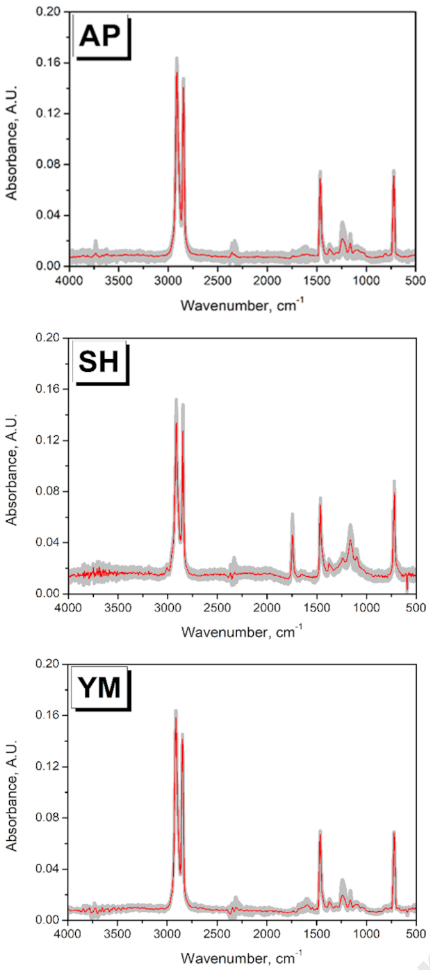

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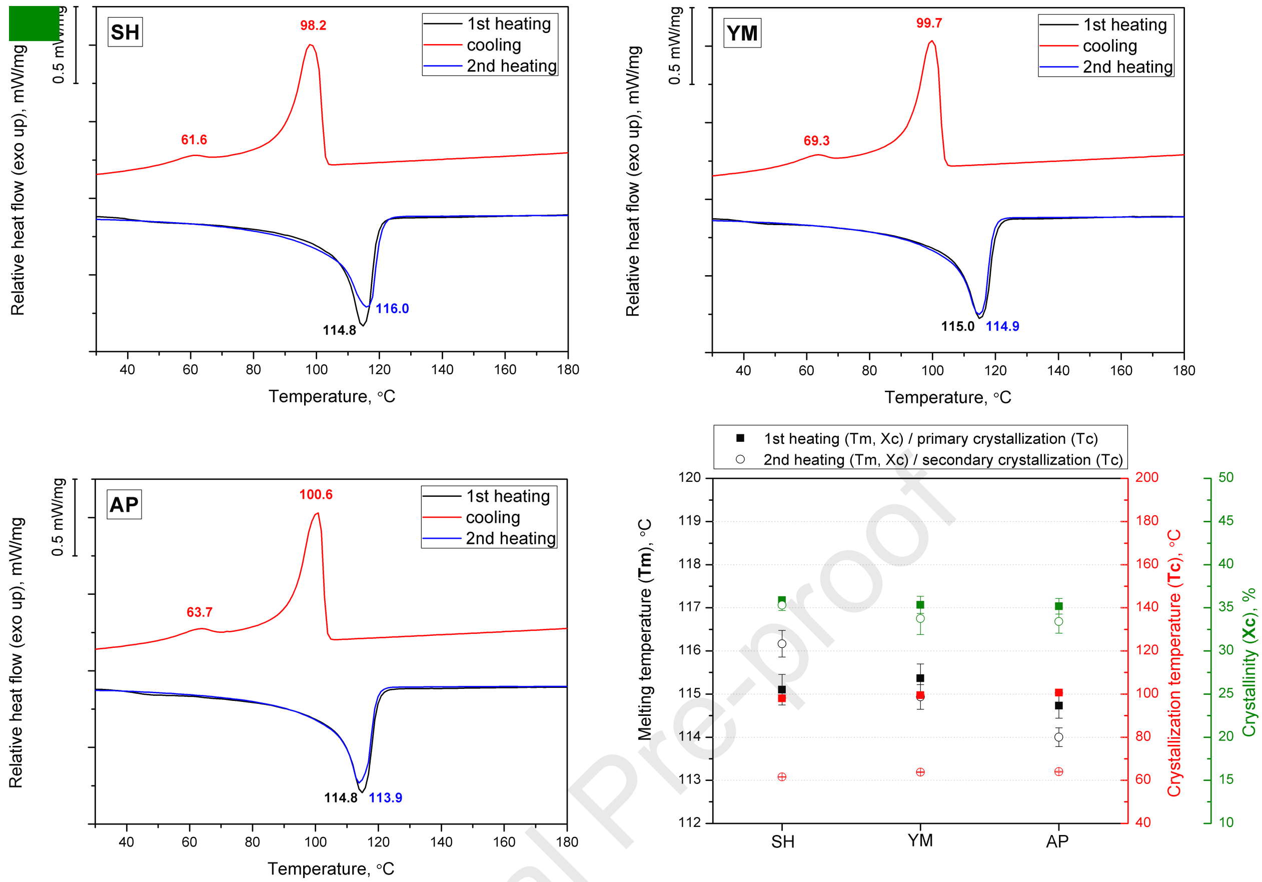

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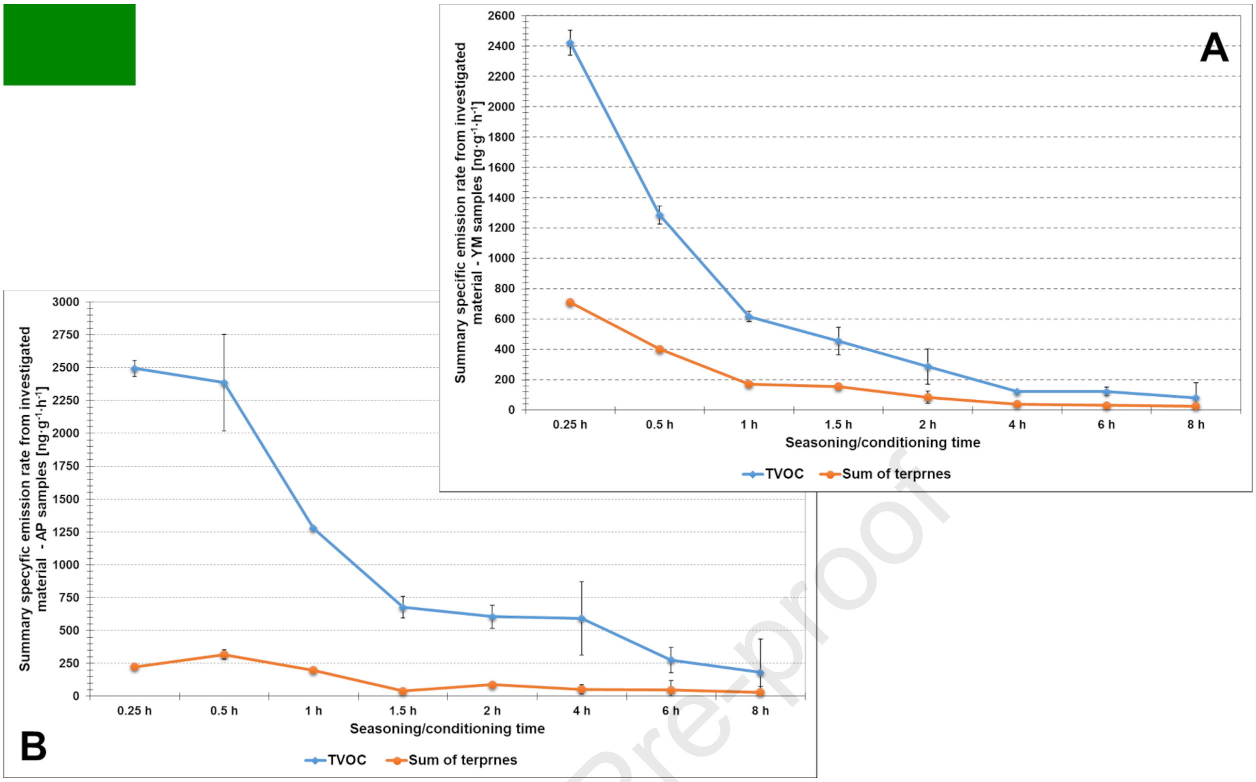

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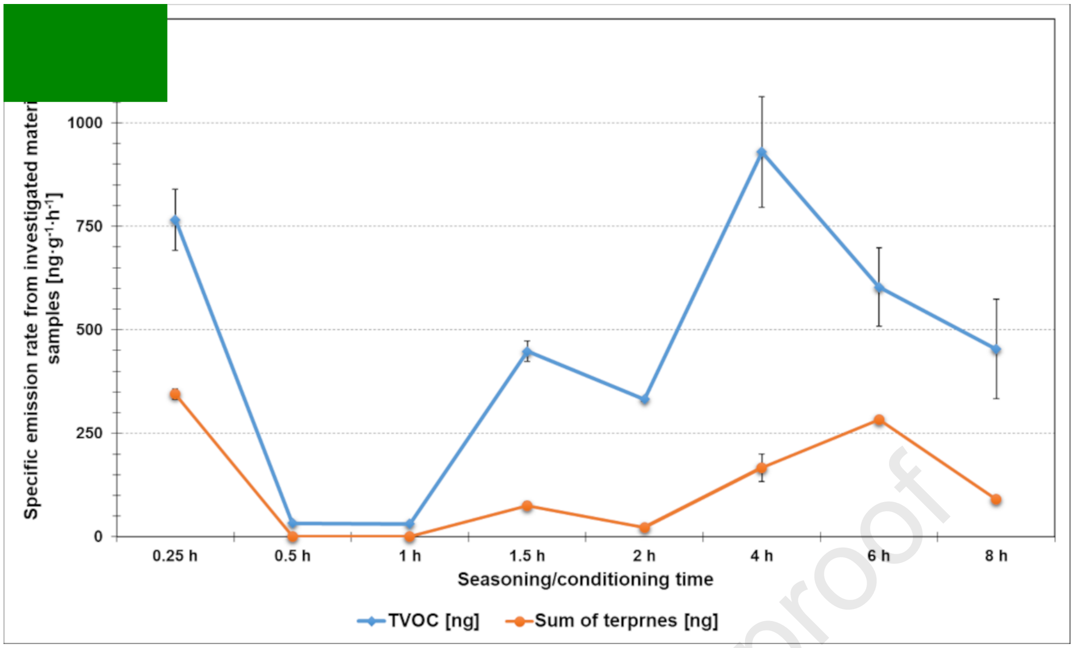

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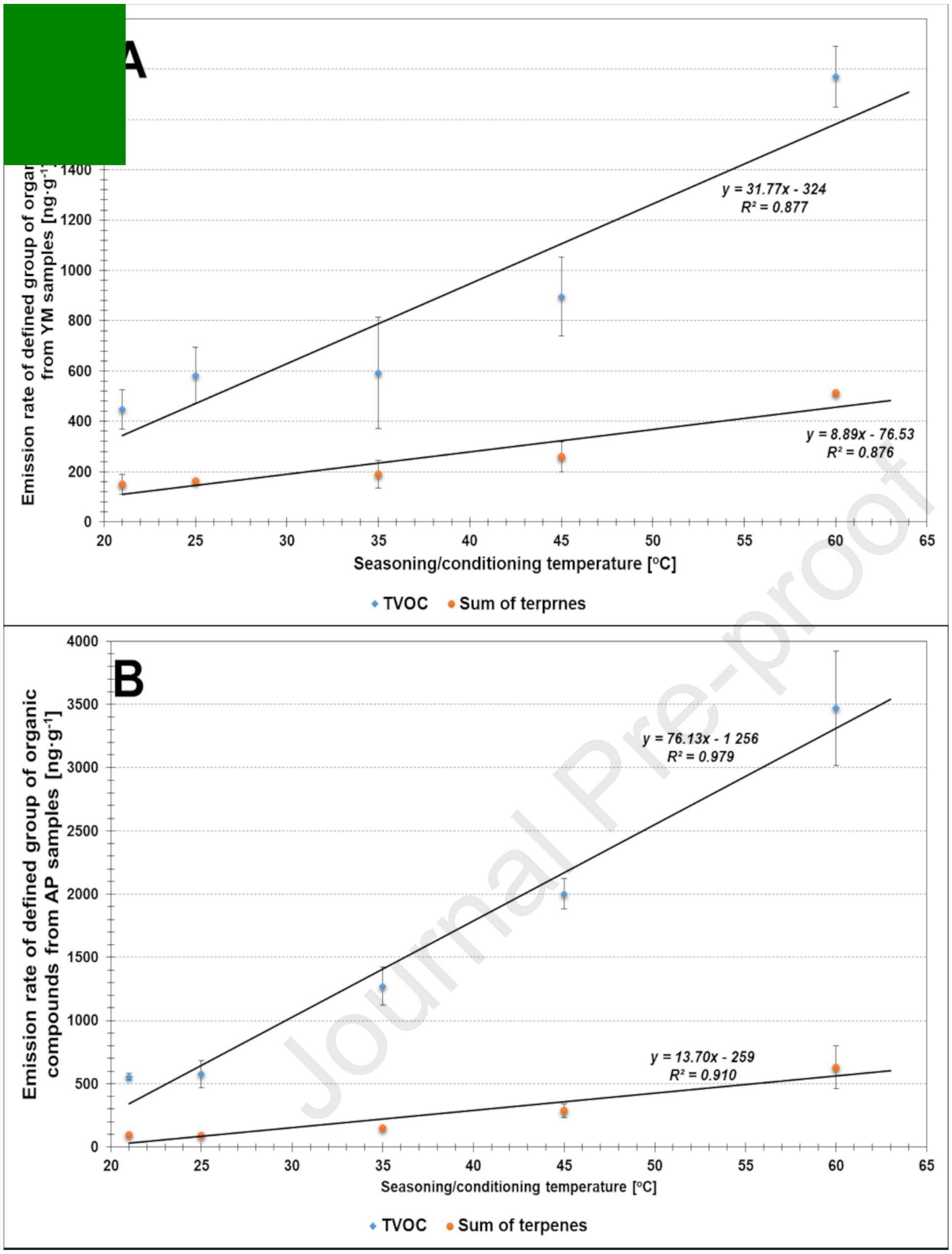

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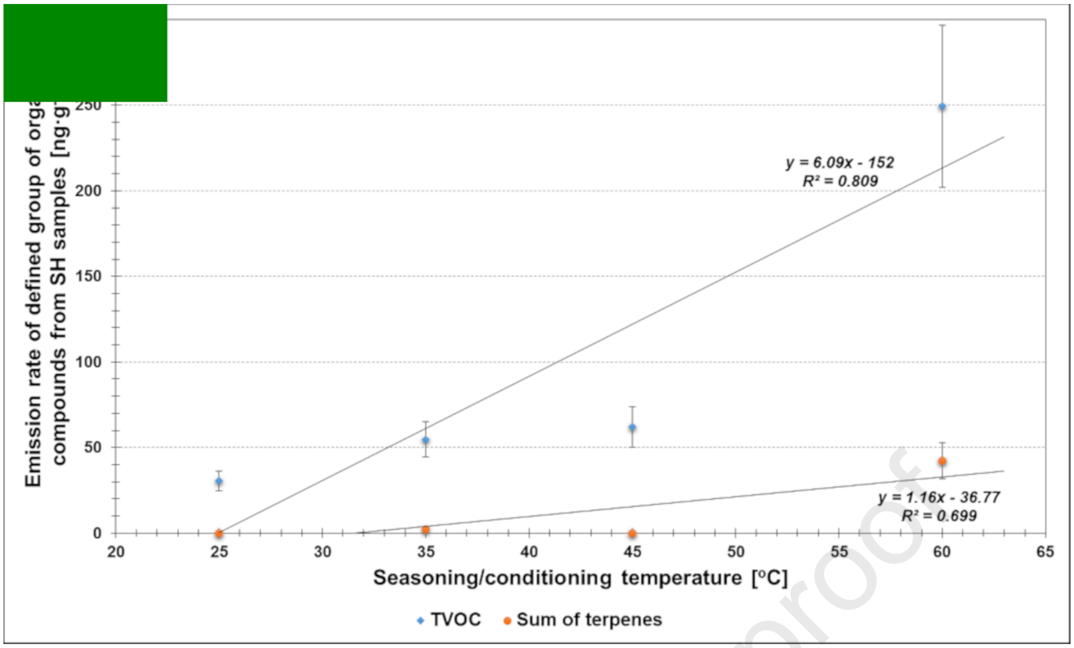

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Highlights

- Candidates for the emission laboratory reference material (LRM) were proposed;
- Apple pomace, sunflower husks, and yerba mate residues were considered as bioadditives;
- Relationship between emission of determined compounds and LRM tests time was investigated;
- Correlation between emission of determined compounds and LRM tests temperature was assessed;
- Developed LRM might be applied in almost every small-scale devices used for the emission tests

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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