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# ELECTROCHEMICAL DETERMINATION OF VOLATILE MARKERS OF BIO-BASED PLASTICS CONTAMINANTS

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**Abstract**

Currently, popular packages, containers and packaging made of biological materials can be a source of undesirable organic contaminants such as total volatile organic compounds (TVOC) and carcinogenic formaldehyde (HCHO). These compounds can easily get into food. The paper presents a proposal to use an original measuring device based on electrochemical sensors DFR-08605 and SGP30 to determine the content of TVOC and HCHO released during heating of the above-mentioned materials. The proposed device was used to monitor HCHO during heating of food contact materials: bio-PET (bio-polyethylene terephthalate), bio-PE (bio-ethylene), EPP (expanded polypropylene) and PLA (polylactide). The obtained results were compared with the results of precise GC-ECD (gas chromatography with electron capture detector) analyses. The possibility of using electrochemical sensors for preliminary analyses of packaging materials was confirmed.

**Keywords**: bio-based materials, electrochemical sensors, formaldehyde, chromatographic analysis.

## 1. Introduction

Petrochemical-derived plastics have gained global popularity due to their unique performance characteristics, which include lightness, transparency, gloss, water barrier, and ease of forming suitable shapes [1]. However, depleting resources of fossil raw materials and global environmental pollution by plastics and microplastics [2, 3] make it necessary to search for alternative sources to produce the desired materials.

Currently, an important criterion for the selection of raw materials is to increase the susceptibility of the final product to biodegradation [4, 5], *i.e.* decomposition under environmental conditions to simple chemical compounds. Various procedures are used for this purpose: modification of the plastic structure by introducing more reactive functional groups into the chain (chemical degradation), adding substances that accelerate photochemical decomposition (photodegradation), or using plant products such as starch and cellulose (can provide a breeding ground for bacteria and fungi – microbial degradation) [6, 7]. New plastics that are more environmentally friendly are called bio-based plastics. These include: *bio-polyethylene terephthalate* (bio-PET), *bio-ethylene* (bio-PE), *expanded polypropylene* (EPP), and *polylactide* (PLA). The raw material for the production of bio-based plastics is mainly plants, *e.g.* bio-PE and bio-PP are made of alcohol extracted from sugar cane, PLA is obtained by bacterial fermentation of starch from corn, beets or potatoes [8, 9].

The global use of plant raw materials for the production of *food contact materials* (FCMs) can be serious food and environment contamination problem. These materials can be contaminated with various undesirable chemical compounds, which can be easily sorbed by plants from the environment (from soil, water and air). Plant materials can also affect the quality


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and sensory properties of served/packed food, as plants contain many volatile, odour-active compounds (such as aldehydes) that shape their specific aroma.

*Formaldehyde* (chemical structure HCHO) is one of the common *volatile organic compounds* (VOC) and polar environmental contaminants [10], which can be easily released from bio-based plastic packaging into food due to its low molecular weight (30 g/mol). This compound is susceptible to thermal degradation over time and at elevated temperatures (about 50-60 °C) [11]. HCHO is characterized by unpleasant, pungent odour, and has an airborne detection threshold of 1 mg/m$^3$ [12].

HCHO is the simplest aldehyde and its identification in a sample can indicate the presence of other odour-active aldehydes, with a more complex structure (Fig. 1). The presence of a mixture of aldehydes in food is not desirable, as they can specifically change the sensory qualities of food, such as coffee [11]. Therefore, HCHO can be a marker of the degree of environmental and the raw material contamination. Its presence allows for a preliminary assessment of the safety of FCMs from the production batch.

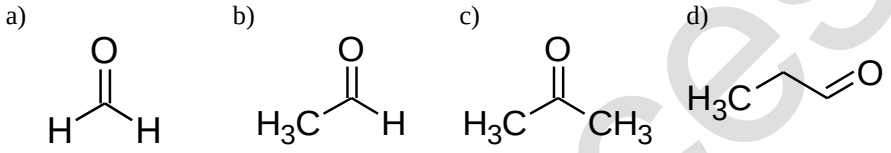


Fig. 1. Semi-structural formulas of formaldehyde (a) and an example of other carbonyl compounds, which belong to volatile organic compounds (VOCs): b) acetaldehyde, c) acetone, d) propanal.

Many methods are popularly used for measuring the concentration of volatile compounds, including HCHO [13]. The chemical reactivity of this compound has influenced the development of a wide range of electrochemical sensors, which are promising solution for quick determination of bio-based plastic contaminants. Three main types of HCHO sensors can be distinguished upon their electrode reaction mechanisms. The first category includes enzymatic sensors, which use biological enzymes to detect HCHO. They based on the highly specific catalytic activity of enzymes. These sensors mainly consist of a working electrode modified with a special enzyme, usually formaldehyde dehydrogenase (FDH), which specializes in catalyzing the oxidation of HCHO. During the oxidation process, electron transfer generates an electric current that is correlated with the concentration of HCHO and can be measured to quantify its presence. The second category includes electrochemical sensors that use electrocatalysts (*i.e.*, metals, oxides, hydroxides, heterogeneous materials) to catalyse the oxidation of HCHO. These sensors are based on the direct oxidation of the target analyte, but the presence of other readily reducible substances can have the effect of introducing interference into the measurement results. Therefore, very important is precise control of the course of the reaction. The third category of HCHO sensors includes electrochemical sensors specific to certain molecules.

In recent years, electrochemical sensors have been widely used in environmental quality control (mainly air) [10, 14-17]. This is due to a number of their advantages, including: real time measurements, simple operation, small size, low energy consumption and costs, easy availability and no preparation of samples for testing. Electrochemical sensors react electrochemically inside the cell, drawing a current proportional to the concentration of the analyte. Modern electrochemical sensors have a high sensitivity (ppb), enabling real-time detection of sensitive pollutants. However, the accurate calibration of such sensors poses significant technical challenges. These include sensor sensitivity to environmental conditions (temperature and relative humidity) [14], moreover cross-sensitivity to other (sometimes unknown or unmeasured) atmospheric factors [14-17] and long-term loss of sensitivity (drift) associated with evaporation of the electrolyte solution.

These limitations make it necessary to calibrate electrochemical sensors before measurements [18-21]. One approach to this issue is to calibrate the electrochemical sensor in the laboratory under a controlled and well-defined range of conditions [22]. Chromatographic techniques, *e.g. gas chromatography with electron capture detector* (GC-ECD), have been widely used for the identification and quantification of HCHO [10, 11]. It allows identification of HCHO at low concentration levels (ng/l). For this reason, it can be successfully used as a reference method for calibrating the readings of electrochemical sensors specific for HCHO.

This paper proposes new applications of commercially available electrochemical sensors for rapid identification and preliminary safety assessment of popular FCMs. A suitable electrochemical device was constructed to measure the concentration of organic contaminants that can be released into food during heating popularly bio-based plastics FCMs, such as: bio-PET, bio-PE, EPP, and PLA. The levels of *total volatile organic compound* (TVOC) and formaldehyde (HCHO as a VOC marker) concentrations were monitored using suitably specific electrochemical sensors. An additional function of the device is to collect air samples for verification using a reference chromatographic method: GC-ECD. The proposed experiment allowed to evaluate the impact of new bio-based plastics FCMs on the quality, stability and sensory properties of food products.

## 2. Construction of the measuring device

Based on the properties of volatile organic compounds (*e.g.* HCHO), the characteristics of the tested FCMs, and according to the experience from our previous work [22], the following assumptions were made for the constructed measuring device:

1) the tested sample after grinding will be heated in a closed jar, and the amount of HCHO and TVOC released will be measured inside the jar to avoid temperature degradation of formaldehyde
2) air from the jar will be passed through electrochemical sensors specific for selected organic pollutants and sorption tubes with XAD-2 insert
3) the validation of the electrochemical sensor readings will be carried out using the reference chromatographic method (GC-ECD) for air samples adsorbed into the sorption tubes
4) 3 identical electrochemical HCHO sensors and 3 identical sorption tubes will be used to determine the accuracy of the electrochemical sensor readings
5) using the device to perform other environmental measurements will be possible.

*DFRobot* DFR-08605 sensors dedicated to measure HCHO, and SGP30 sensors dedicated to measure TVOCs were used in the designed device [23, 24]. The proposed device consists of two parts: measuring probe and the main module. These components additionally control the operation of an external heater for heating the jar with the tested sample. The general diagram of the device construction is presented in Fig. 2. and the view of the final device is shown in Fig. 3.

### *2.1. Measuring probe*

The measuring probe (no. 1 in Fig. 3a) is mounted on the measuring jar and connected to the main module using electrical wires (no. 2 in Fig. 3a). The jar is closed with a cap (no. 3 in Fig. 3a). The probe contains three HCHO DFR-08605 (no. 4 in Fig. 3a) sensors and two TVOC sensors (below them). Additionally, a DHT22 temperature and humidity sensor (no. 5 in Fig. 3a) is installed, which enabled to control the temperature of the tested sample. There are also three connectors (no. 1 in Fig. 3b) for standard sorption tubes (no. 2 in Fig. 3b) with a diameter of 8 mm and length of approx. 100 mm each on the back of the probe. A polyurethane pneumatic hose with an external diameter of 4 mm (no. 6 in Fig. 3a) is connected to each of the

connectors. Fourth hose (no. 3 in Fig. 3b) allows the air to circulate in the jar (when air is not pumped through the sorption tubes).

The probe and the main module were 3D printed from PET-G. This material does not release any substances or emit any odour, so it should not affect the quality of the obtained measurement results.

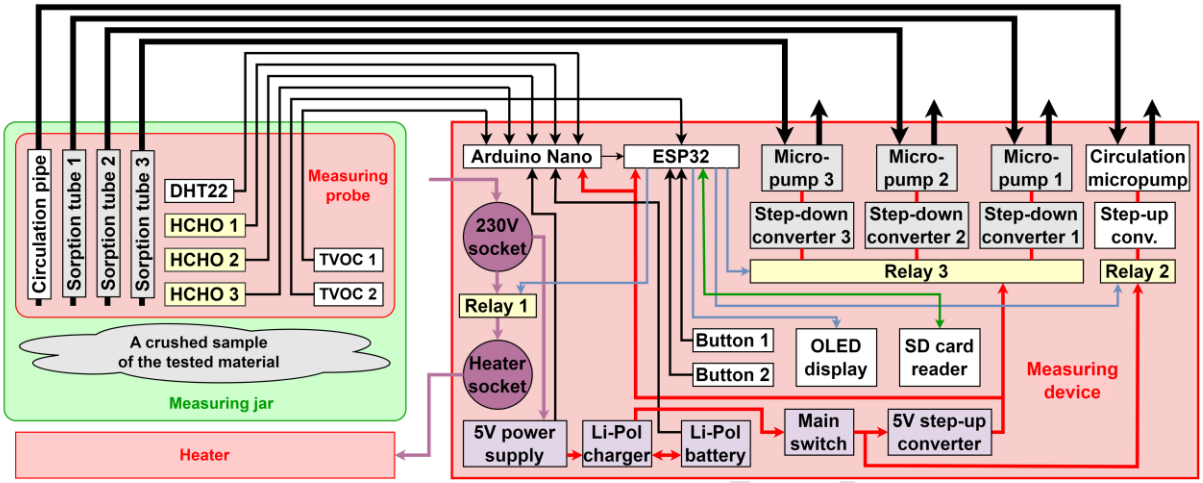


Fig. 2. Construction diagram of the measuring device.

a) b)

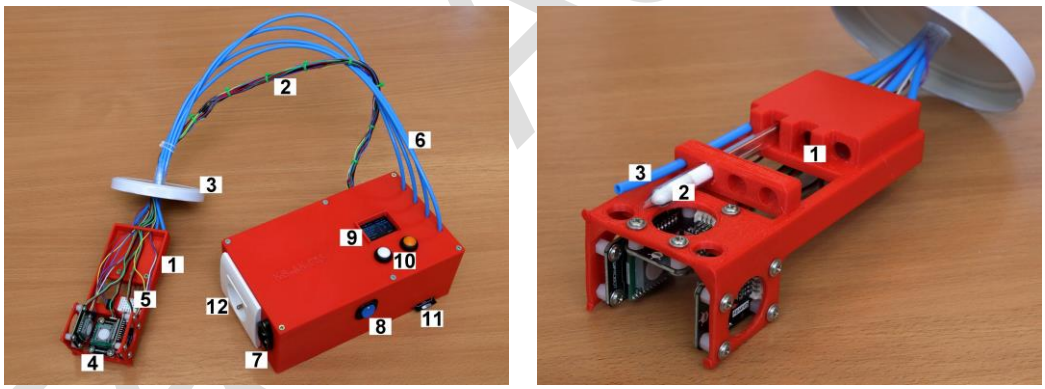


Fig. 3. Measuring device: a) overall view, b) bottom of the measuring probe.

## *2.2. Main module*

The main module is powered by 230 V from the mains socket (no. 7 in Fig. 3a) or by a built-in *Akyga* 3.7 V, 4 Ah Li-Pol battery (for measurements performed outside the laboratory). The module is turned on by the switch marked no. 8 in Fig. 3a. The air flow through the sorption tubes and the circulation tube is provided by 4 separate mini vacuum pumps SC301P switched by relays. The circulation pump provides an air flow of 355 ml/min through the circulation hose. Three regulated step-two converters supply the remaining sorption pumps. Thanks to this, each sorption pump provides an air flow equal to 1/3 of the flow of the circulation pump (*i.e.* 118.3 ml/min). Therefore, switching the circulation pump to the sorption pumps does not affect the air circulation in the measuring jar and the sensor readings. The main module is controlled by the ESP32-DevKitC development board. Several elements are connected directly to it:

1) OLED screen (to view measurement data and device settings – no. 9 in Fig. 3a)

2) 2 momentary buttons to control the device (no. 10 in Fig. 3a)
3) reader of popular SD memory cards for recording measurement data (no. 11 in Fig. 3a)
4) 4-channel relay module; three relays were used: 1 – to control the heater of the measuring jar, 2 – to control the circulation pump, 3 – to control the sorption pumps
5) one of the TVOC sensors
6) Arduino Nano development board, connected to:
   a) 3 HCHO sensors
   b) the second of the TVOC sensors
   c) DHT22 sensor measuring temperature and relative humidity.

In addition, 2 analogue inputs of the Arduino Nano were used to measure the battery voltage and check the connection of the 230 V mains voltage. Measurements are performed every 4 seconds (in each measurement cycle, 10 HCHO sensor readings are averaged).

### *2.3. External heater*

The main module is designed to control an external heater powered by 230 V mains voltage. The heater is connected to the socket (no. 12 in Fig. 3a) and left in the on position. A heater with a maximum power of about 2 kW can be used due to the load capacity of the contacts of the applied relay of 10 A. During the experiments, an 800 W heater was used.

### *2.4. Device functionality*

The view of the designed device at the laboratory stand is shown in Fig. 4a. The ESP32 and Arduino Nano software was developed in a dedicated Arduino development environment. Communication with the user is carried out using the two buttons and the screen. The information shown in Fig. 4b is displayed, after switching-on the device. The right part shows the readings from the sensors. Formaldehyde and TVOC concentrations are given in ppb.

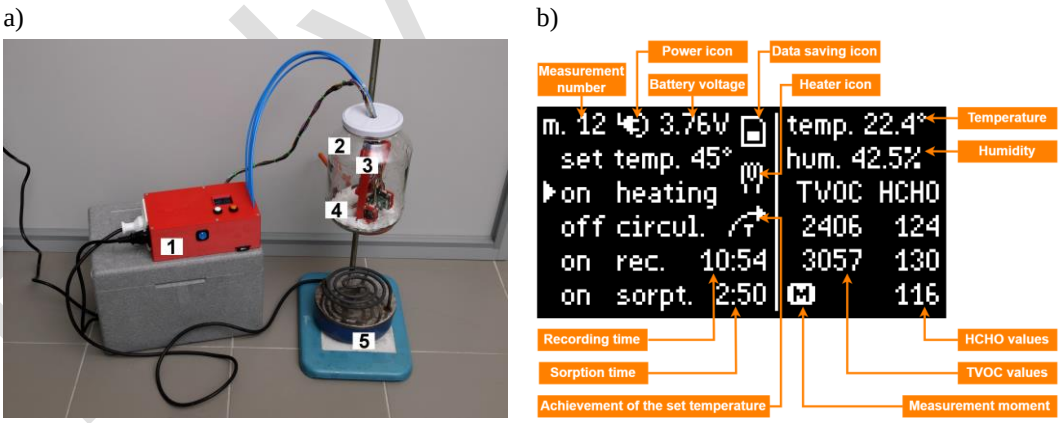


Fig. 4. a) Our device at the laboratory stand: 1 – measuring device, 2 – measuring jar, 3 – measuring probe, 4 – tested material, 5 – heater, b) Information displayed on the main module screen.

The current measurement series number displays on the upper left corner and the mains power icon and battery voltage on the right side, respectively. There are 5 functions selected in sequence with the left button below it. The first one is the heating temperature selection. It can be changed with the right button in the range of 25~50 °C in 5 °C steps. The second function is to turn-on the heating mode. The “Heater icon” on the right indicates that the heater is turned-on. Below it is the “Achievement of the set temperature” icon. The third function is to turn-on the circulation pump. Its use is necessary for conducted the measurements when the probe is

placed in a closed measuring jar. The fourth function starts the recording of the measurement data onto the memory card. The time of data recording in minutes and seconds is shown with the time counter on the right. The moment of recording is indicated by the upper icon “Data saving icon”. In addition, the lower icon “Measurement moment” indicates the reading of data from the sensors. The fifth function is to start the sorption pumps. Their operating time in minutes and seconds is shown with the timer on the right.

The first two functions (related to the heater operation) are available only when the main module is connected to the mains power supply. Otherwise, the message “No AC power” is displayed in their places. Similarly, the last two functions are available only when a writable SD card is detected in the card reader. The lack of the card is indicated by the message “No SD card” displayed in their places.

### *2.5. Saving measurement data*

Measurement data is saved on the SD card in CSV text files. Each line contains data from the next reading separated by semicolons. File names are in the form 'data-xx.csv', where xx is the two-digit number of the measurement series started in the next step. This number is displayed in the upper left corner of the screen. The following parameters are saved in each line of data: measurement series number, connecting or not connecting to the mains power, value of the set heating temperature, turning-on or -off the heating mode, turning-on or -off the heater, pump status, current measurement recording and pumping times, temperature and relative humidity, readings from HCHO DFR-08605 sensors, readings from SGP30 sensors.

### *2.6. Heating algorithm*

Quickly achieving and precisely maintaining the set temperature ($t_s$) in the jar is a difficult task. It is related to the following reasons:

1) placement the heater at a certain distance from the jar to prevent from cracking it
2) the high thermal capacity of the glass jar
3) slow heating of the air in the jar from its heated walls
4) operation (or not) of pumps cooling the air in the jar.

For this purpose, an algorithm was developed that minimizes the time required to establish the set temperature, prevents its overshoot and maintains it as precisely as possible for the duration of the measurements. For the two-level control of the heater using relay no. 1, we use the current temperature ($t_c$) read from the DHT22 sensor and analyse its changes in 30-second intervals ($t_p$ – previous temperature). The algorithm's flow chart is shown in Fig. 5.

The effectiveness of the proposed algorithm was confirmed in the experiments presented in the next section. In all cases, the temperature was maintained within ±2 °C of the set temperature.

## 3. Experiment based on proposed measuring device

### *3.1. Determination of volatile markers by electrochemical sensors*

The proposed device was used to monitor the concentration of TVOCs and HCHO that can be released during heating of the popularly used bio-based plastic FCMs: bio-PET, bio-PE, EPP, and PLA. The measuring device was heated for 4 hours to release HCHO and other TVOCs from the jar cap and the elements used to build the measuring probe, before starting the actual measurements. A blank test (heating an empty jar) was also carried out. In order to monitor the concentration of TVOCs and HCHO released from the currently popular bio-based

plastics, the analysed FCMs were cut and introduced into the jar in the following amounts: bio-PET – 30 g, bio-PE – 10 g, EPP – 30 g and PLA – 60 g. Then the device was turned-on with the following settings: heating temperature: 50 °C, circulation pump on and recording of measurement data from the beginning of the experiment. Data from electrochemical sensors were collected for about 40 min. For the air sorption time, the average HCHO concentration measurements were determined and compared with the results obtained using the reference chromatographic method.

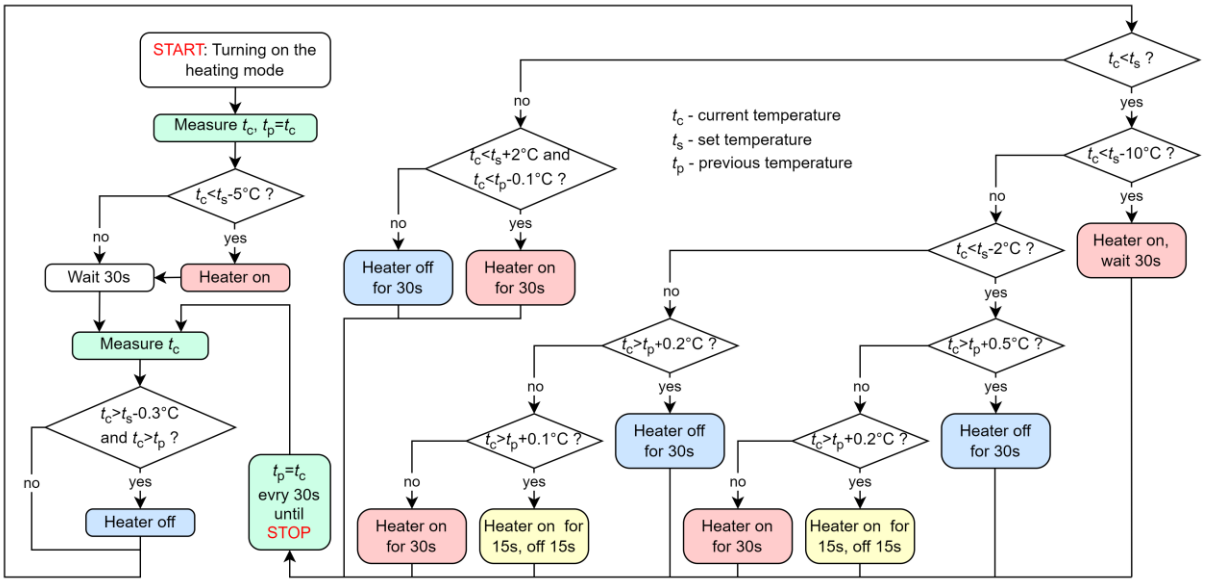


Fig. 5. Heater control algorithm.

### *3.2. Determination of volatile markers by chromatography (reference method)*

In order to assess the accuracy of the readings of the electrochemical sensors specific for HCHO, samples were collected for the reference GC-ECD analysis. Three replaceable sorption tubes with XAD-2 bed (three replicates for each sample) were placed in the device for this purpose. After stabilizing the temperature (50 °C), the vapours emitted from the heated FCMs were sorbed into the sorption tubes at a flow rate of 118.3 ml/min (per tube) for 5 min.

Sample preparation for GC-ECD chromatographic analysis includes several steps: desorption of gas samples from the sorption tube bed using 2 ml of methanol; derivatization process using 2,3,4,5,6-*pentafluorobenzylhydroxylamine* (PFBOA) at a concentration of 2 mg/ml; *Liquid-Liquid Extraction* (LLE) with hexane and purification. A detailed description of sample preparation for GC-ECD analysis can be found in our previous works [10, 11, 22].

Low-molecular weight carbonyl compounds (*e.g.* HCHO and others) were analysed using the *Fisons Instruments* 8000 equipped with $^{63}$Ni electron capture detector (GC-ECD). Injections of 0.5 µl of the extract were introduced via "on column" injector into chromatographic column. A Rtx-5MS (*Restek*) fused silica capillary column (30 m × 0.25 mm × 0.25 µm film thickness) was employed for analysis, and a Rtx-1301 (*Restek*) fused silica capillary column (30 m × 0.32 mm × 0.5 µm film thickness) was used as a confirmation column. Injector temperature was set at 80 °C. Gas flow was set at 80 kPa. Helium was used as carrier gas and nitrogen was used as make-up gas for the detector. Analysis was carried out on a temperature program starting at 80 °C for 4 min, then increasing the temperature to 240 °C with an increase of 7 °C/min, and then to 290 °C with an increase of 20 °C/min. *DataApex*, *Clarity* 6.2, Czech Republic software was used to collect and process chromatographic data.

Quantification of contaminants was carried out using an external standard calibration curve. All standards were prepared gravimetrically with a concentration range of 4-100 µg/l. The precision of the method was evaluated in terms of repeatability and expressed as relative standard deviation (RSD %). The analytical parameters for HCHO are shown in Table 1.

Table 1. Chromatographic parameters for HCHO.

| **Retention time (min)** | **5.82** |
|---|---|
| Standard curve equation | $y$=38(±2)$x$ + 2011(±185) |
| Limit of detection (LOD) (µg/l) | 0.003 |
| Limit of quantification (LOQ) (µg/l) | 0.009 |
| Relative standard deviation (%) | 1.7 |

## 4. Results and discussion

### *4.1. Electrochemical approach*

The proposed measuring device allows rapid electrochemical determination of TVOCs and HCHO released from bio-based plastics. Fig. 6 compare the concentrations of TVOCs and HCHO released over time (for about 40 min) from bio-PET, bio-PE, EPP and PLA at increasing temperature (to 50 °C). Based on the conducted study, it was observed that all analysed bio-based plastic FCMs can be a source of TVOCs and HCHO release into heated food. The use of an electrochemical sensor allowed to determine the trends of release of these organic pollutants.

Thermal degradation reactions of bio-based plastics or additives stabilizing packaging occur during heating of materials. TVOCs and HCHO can be reaction products. However, simple organic compounds are also thermally unstable and can decompose at elevated temperatures. These two processes occur simultaneously and have a significant impact on the final concentration of TVOCs and HCHO, which are detected by electrochemical sensors.

An increase in the concentration of TVOCs and HCHO is observed at the beginning of heating. It means that the thermal decomposition processes of bio-based plastics and additives occur faster than the degradation of analytes. This is particularly clearly visible in Fig. 6a. For the first approx. 18 min of heating bio-PET, an increase in the HCHO concentration to approx. 750 ppb was noted. The HCHO concentration stabilizes with further heating of this biomaterial (from 18 min to approx. 22 min). It may indicate that an equilibrium has been established between the rate of the degradation reaction of bio-based material and additives and the decomposition of HCHO. Longer heating (over 22 min) may lead to a decrease in the HCHO concentration (to approx. 200 ppb). Probably only the degradation processes of the formaldehyde produced occur at this stage. Similar trends can be observed for TVOCs (Figs. 6b, 6d, 6f and 6h).

The trends of increase, stabilization and decrease of TVOCs and HCHO concentrations may occur at different times, temperature and concentration levels, depending on the materials. In general, the highest concentrations of HCHO can be released from bio-PET at 43-48 °C (>700 ppb), from bio-PE from 22-28 °C (>150 ppb), from EPP from 24-30 °C (>200 ppb) and from PLA from 34-40 °C (>400 ppb). The source of carcinogenic formaldehyde may be the thermal degradation process of polymers [25-27].

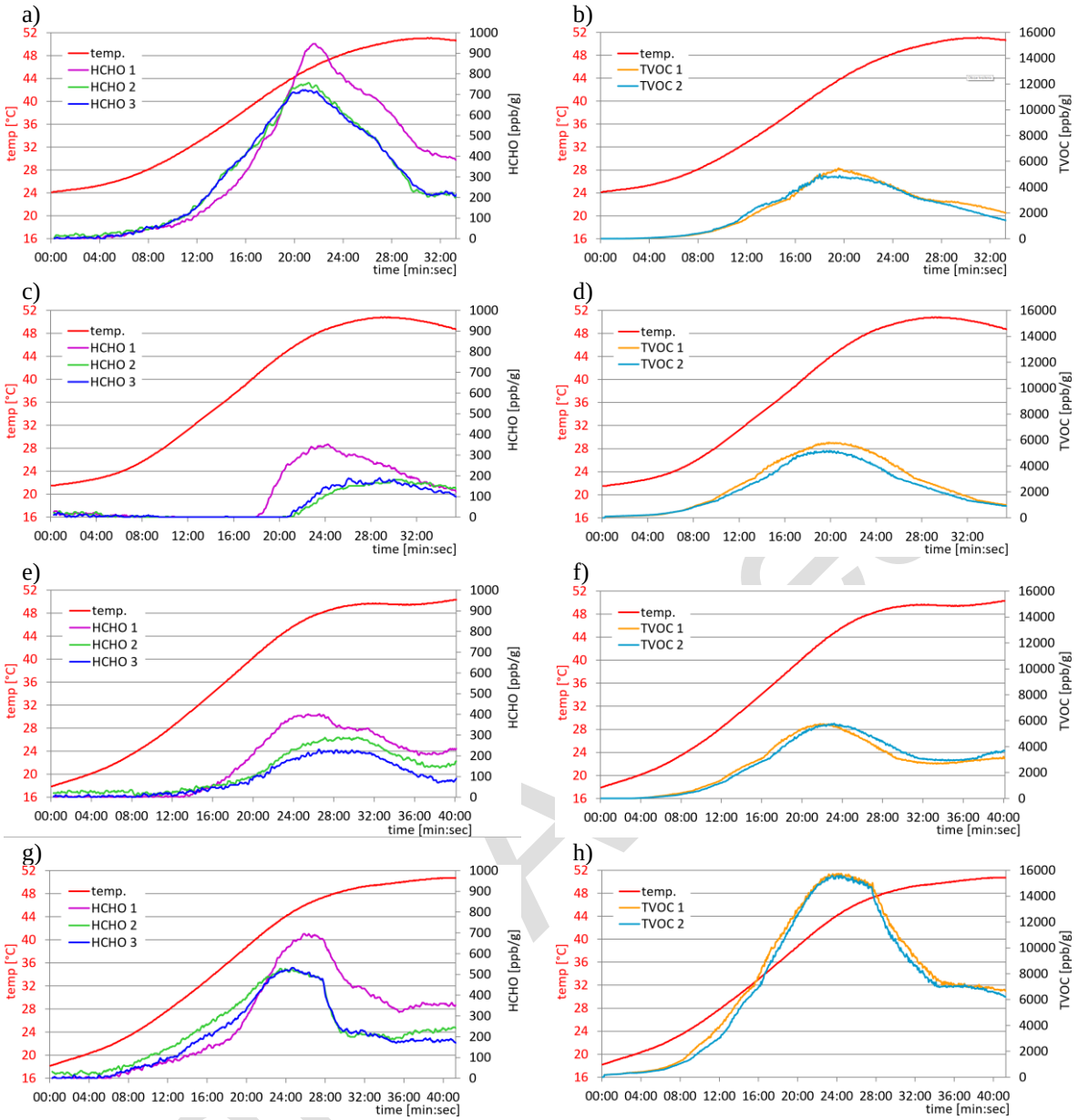


Fig. 6. Results of determination of volatile markers using electrochemical sensors (expressed in µg/kg of material): a) HCHO from bio-PET, b) TVOC from bio-PET, c) HCHO from bio-PE, d) TVOC from bio-PE, e) HCHO from EPP, f) TVOC from EPP, g) HCHO from PLA, h) TVOC from PLA.

In contrast, the highest concentrations of TVOCs can be released from PLA at 48-52 °C (~15000 ppb). For the other materials, comparable highest concentrations of TVOCs were recorded at about 28 °C (~6000 ppb). The odour active compounds include aldehydes, ketones, carboxylic acids, alcohols and lactones, which are probably detected by the applied electrochemical sensor [28]. The amount of TVOCs released is strongly correlated with temperature. PLA is classified as a heat-shrinkable material and melts at an elevated temperature (50 °C). Therefore, the thermal degradation processes of the polymer occurred faster for this sample, which could have influenced the higher concentration of TVOCs released from this material. Characteristic TVOCs for PLA include mainly compounds from the aldehyde group (*e.g.* octanal, 3-nonenal, 3,6-nonadienal, nonanal, citronellal, (E)-2-nonenal, dodecanal) and ketones (*e.g.* 1-octen-3-one, 3,5-octanedione, sotolon) [28]. In turn, VOCs specific to EPP material may include 2,2-dimethylpentane, 1,1,3-trimethylcyclopentane, 2-methyl-2,3-hexadiene, 3,6-dimethyldecane, glycerine, 2-chlorophenyloxirane, diethyl

phthalate, benzophenone and docosane [29]. In turn, acetaldehyde, glycol, nonanal and 2-methyl-1,3 dioxolane was noted as TVOCs characteristic for bio-PET and bio-PE material [30, 31].

### *4.2. Reference (chromatography) approach*

HCHO concentration values obtained by electrochemical and chromatographic (GC-ECD) methods were compared to determine the accuracy of the electrochemical sensors used. Table 2 shows the average values of HCHO concentrations that were measured by the two methods (under the same measurement conditions). In the case of the chromatographic analysis, the calculations took into account the flow of gaseous samples through the sorption tubes (118.3 ml/min), the sorption time (5 min), the sample enrichment due to the desorption of 2 ml of methanol (295.75 times), the recovery (98 % for HCHO) and the weight of the sample FCMs. The results obtained take into account blank samples.

In turn, Table 3 shows the mean values and variances of TVOC concentrations obtained from SGP30 sensors over the same time ranges.

Table 2. Average formaldehyde concentrations (µg/kg of material) from individual HCHO sensors and from GC-ECD analysis.

| Sensor | bio-PET | bio-PE | EPP | PLA |
|---|---|---|---|---|
| HCHO 1 | 619 | 278 | 307 | 373 |
| HCHO 2 | 411 | 156 | 256 | 204 |
| HCHO 3 | 415 | 169 | 198 | 196 |
| HCHO sensors averaged | 482 | 201 | 254 | 258 |
| variance of HCHO sensors | 9427 | 2988 | 1954 | 6677 |
| GC-ECD averaged | 258 | 268 | 209 | 118 |

Table 3. Average TVOC concentrations (µg/kg of material) obtained from individual electrochemical sensors.

| Sensor | bio-PET | bio-PE | EPP | PLA |
|---|---|---|---|---|
| TVOC 1 | 3050 | 3187 | 2832 | 8094 |
| TVOC 2 | 2869 | 2624 | 3236 | 7623 |
| TVOC sensors averaged | 2959 | 2905 | 3034 | 7858 |
| variance of TVOC sensors | 8176 | 79276 | 94287 | 55448 |

Based on the obtained results (Table 2), it can be seen that the average readings of the electrochemical sensors are higher than the HCHO concentrations determined by the reference method (GC-ECD). The differences in the readings are significant, especially for bio-PET and PLA. The electrochemical sensors overestimate the concentrations of released HCHO by almost two times for this samples. The reason for the discrepancy may be the presence of other carbonyl compounds in the analysed samples, with a structure similar to HCHO. This means that the *DFRobot* DFR-08605 sensors are characterized by cross sensitivity and misread other compounds as HCHO. Chromatographic analysis confirmed this suspicion, as other low molecular weight aldehydes and ketones were identified in the analysed samples (including acetaldehyde, acetone, propanal, butanal, pentanal and benzaldehyde) (Fig. 7).

Lower readings of HCHO concentration recorded by electrochemical sensors than by the reference method were observed only for bio-PE. This may probably be related to the particularly rapidly increasing values of the released HCHO, which resulted in exceeding the maximum increases recorded by the sensors.

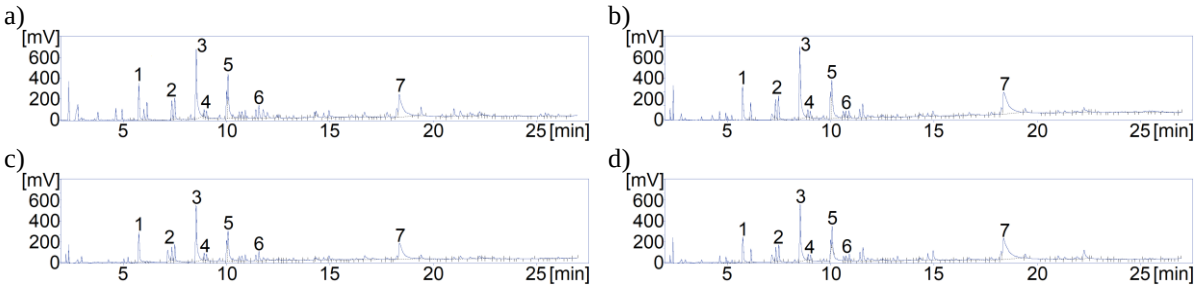


Fig. 7. GC-ECD chromatograms obtained for the analysed bio-based plastic FCMs: a) bio-PET, b) bio-PE, c) EPP, d) PLA. Identification of carbonyl compounds: 1 – formaldehyde, 2 – acetaldehyde, 3 – acetone, 4 – propanal, 5 – butanal, 6 – pentanal and 7 – benzaldehyde.

For these reasons, the *DFRobot* DFR-08605 sensors can be used for the determination of total carbonyl compounds, rather than for specific HCHO analysis. They can be used as a preliminary method for assessing the safety of bio-based materials, since HCHO can be treated as a marker for the presence of other, low-molecular-weight carbonyl compounds. In addition, the use of TVOCs sensors provides a preliminary estimate of the amount of volatile odour compounds released from heated bio-based plastics FCMs. In addition, low variance values were obtained for most of the results, as can be seen from Tables 2 and 3. This demonstrates the consistency and similar quality of the readings of the electrochemical sensors used.

Pearson correlation coefficients were calculated to determine the consistency of HCHO and TVOC sensor readings. They were calculated for values recorded by the sensors during the entire duration of individual measurements. The obtained results are summarized in Table 4. Additionally, Pearson correlation coefficients were calculated between the averaged readings of the HCHO and TVOC sensors. They are placed in the last row of Table 4.

Table 4. Pearson correlation coefficients for HCHO 1-3 and TVOC 1-2 sensors and between averaged HCHO and TVOC sensor readings.

| **Sensors** | **bio-PET** | **bio-PE** | **EPP** | **PLA** |
|---|---|---|---|---|
| HCHO 1-2 | 0.942 | 0.708 | 0.957 | 0.841 |
| HCHO 1-3 | 0.940 | 0.806 | 0.959 | 0.891 |
| HCHO 2-3 | 0.997 | 0.968 | 0.979 | 0.986 |
| TVOC 1-2 | 0.989 | 0.996 | 0.984 | 0.998 |
| HCHO-TVOC | 0.957 | 0.219 | 0.774 | 0.977 |

Obtaining Pearson correlation coefficient values close to 1, especially for HCHO 2 and HCHO 3 sensors and TVOC 1 and TVOC 2 under the same, controlled conditions, proves their precise design and similar sensitivity and accuracy for the tested formaldehyde. It also indicates that in further studies of a similar nature there is no need to multiply the electrochemical sensors of the same type. The differences in the readings obtained (visible between HCHO 1 and HCHO 2 sensors) may be the result of the non-uniformity of the distribution of the samples of the tested material, which requires further analysis. The demonstrated differences in the readings of HCHO sensors and GC-ECD analysis prove that such sensors require calibration before use.

## 5. Conclusions

The global popularization of new, bio-based plastics food contact materials (FCMs) makes it necessary to search for methods to assess their safety. This paper presents the design and operation of a measuring device based on electrochemical sensors (*e.g. DFRobot* DFR-08605), which can be used as a fast, low-cost, easily accessible and environmentally friendly method

for pre-testing the safety of FCMs to confirm or exclude health and environmental risks. In order to determine the accuracy of the electrochemical sensor readings, the results obtained by the electrochemical method were compared with the reference chromatographic method (GC-ECD). Based on the study, it was observed that some FCM bioplastics can be a source of release of carcinogenic formaldehyde (HCHO) and volatile organic compounds (TVOC) into food when heated (up to 50 °C). The type of FCMs and the heating temperature have a strong influence on the amount of organic contaminants released. Some simple chemical compounds are susceptible to thermal degradation. Furthermore, it was observed that the readings from the *DFRobot* DFR-08605 sensor were overestimated compared to the reference method (GC-ECD), which is probably due to the cross-sensitivity of this sensor. Pearson correlation analysis showed high agreement between readings from the same type of sensor, indicating good reproducibility of the results obtained. In summary, presented sensors can be used in "screening measurements" that will allow for the fast determination of contamination markers characteristic for specific materials. They can also be used in more advanced devices designed to assess the safety of other environmental matrices (soil, water, plants) in the future.

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