Food Chemistry 392 (2022) 133290

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

A new sensor for direct potentiometric determination of thiabendazole in fruit peels using the Gran method

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ARTICLE INFO

Keywords:
Thiabendazole
Potentiometric sensor
Ion-selective membrane
Direct potentiometry
Gran method

ABSTRACT

A new sensor for direct potentiometric determination of thiabendazole (TBZ) was prepared. The ionic pair of TBZ cation and the 5-sulfosalicylate anion was used as the new sensor material incorporated in liquid type of ion-selective electrode membrane for TBZ determination. For optimization of the membrane of the sensor for TBZ determination, six different plasticizers and the content of the sensor material in the membrane were varied. The chosen sensor with dibutyl sebacate (DS) as plasticizer and 1% of sensor material in the membrane was characterized with Nernstian response towards TBZ (62.2 mV/decade of activity), a wide working range ($8.6 \bullet 10^{-7}$–$1.0 \bullet 10^{-3}$ M), and a low limit of detection ($3.2 \cdot 10^{-7}$ M). Also, it proved to be an accurate and reliable sensor for TBZ determination in pure and real samples (peel of oranges, lemons and bananas) where it was determined using direct potentiometry and Gran method.

1. Introduction

Citrus fruits are an excellent source of nutrients such as vitamin C, flavonoids, and fibers which makes them very popular in human diet. Among them, oranges and lemons have the highest commercial importance (Liu et al., 2012). According to European Commission, in 2020/21 the annual European production of all citrus fruits was about 11.4 million tones, lemons about 1.7 million tones, and oranges about 6.4 million tones (Citrus fruit statistics | European Commission., 2021). Bananas are also one of the most popular fruits worldwide. They contain phenolics, carotenoids, biogenic amines, and phytosterols, which have positive effects on human health (Singh et al., 2016). According to European Commission, in 2020/21 the annual European production of bananas was about 640.000 tonnes (Bananas statistics | European Commission., 2022). Citrus fruits, as well as bananas, have poor shelf life (Kosseva et al., 2016). Because of that, and in order to prevent post-harvest looses, use of pesticides, such as thiabendazole (TBZ), is unavoidable.

TBZ is benzimidazol pesticide. Its chemical structure is presented in Fig. S1. TBZ can be applied both, preharvest and post-harvest to protect fruit and vegetables from fungal diseases, and to avoid their deterioration during storage and transport. In USA and Europe, it is one of the most frequently detected pesticides in agri-food products (Estevez et al., 2012). Due to its wide application, the residues of TBZ can be found in fruit and vegetables (mostly in their peel), as well as in their products. Considering the stability of TBZ in food processing procedures (Tsialla et al., 2015), it can be expected that TBZ can pass to the human body. Although it is characterized by low acute toxicity, US Environmental protection agency (EPA) classified TBZ as likely to be carcinogenic at doses high enough to cause disturbance of the thyroid hormone balance (United States Environmental Protection Agency, 2002). Also, it is related to nephrotoxic, teratogenic, and hepatotoxic adverse effects and binds to human serum albumin (Yang et al., 2015). Due to these facts, TBZ monitoring is an essential task in order to ensure food safety. Considering wide application of TBZ on citrus fruits, and bananas, the European food safety authority defined the maximum residue level for TBZ as 7 mg/kg in citrus fruits and 6 mg/kg in bananas (Anastassiadou et al., 2021).

Abbreviations: TBZ, thiabendazole; SAL, 5-sulfosalicylic acid; THF, tetrahydrofuran; PVC, polyvinyl chloride; *o*-NPOE, *o*-nitrophenyloctylether; BEHS, bis(2-ethylhexyl) sebacate; DBP, dibutyl phthalate; NPPE, 2-nitrophenyl phenyl ether; DS, dibutyl sebacate, DOP, bis(2-ethylhexyl) phthalate; LOD, limit of detection.

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https://doi.org/10.1016/j.foodchem.2022.133290
Received 8 October 2021; Received in revised form 20 May 2022; Accepted 20 May 2022
Available online 21 May 2022

Various analytical methods such as high-performance liquid chromatography (Yu et al., 2017), ultra-performance liquid chromatography (Zhan et al., 2020), gas chromatography (Machado et al., 2017), immunoassay (Tsialla et al., 2015), surface-enhanced Raman spectroscopy (Wang et al., 2021), UV/Vis spectrophotometry (Tuzen et al., 2021), phosphorimetry (Piccirilli & Escandar, 2009), fluorimetry (Kazemifard et al., 2020), and chemiluminescence (Asghar et al., 2016) have been used for TBZ determination in different samples. However, most of these methods require expensive instrumentation, complicated analytical procedures, time-consuming sample preparation, and consumption of toxic organic solvents. Therefore, it is necessary to develop simple and low-cost but still accurate, sensitive, and selective analytical method or sensor for TBZ determination. Potentiometry and ion-selective electrodes (ISEs) with liquid membrane, as detectors for the potentiometric determination of TBZ, represent a promising and reliable alternative (Volnyanska et al., 2020). The membranes of ISEs, which are responsible for their selectivity and sensitivity, usually consist of polyvinyl chloride, plasticizer, and an ionophore as the sensing material. As sensing material, which is responsible for response of the sensor, new functionalized materials such as metal–organic frameworks (Wagner et al., 2021) and multi-walled carbon nanotubes (Budetić et al., 2021) can be used. Besides the ionophore, the type of plasticizer also has an impact on the response of the ISE, as well as on its life time (Sakač et al., 2021; Zahran et al., 2010; Zahran et al., 2014). Considering the above, by varying the membrane components, it is possible to develop ISE with improved analytical characteristics such as wider measuring range, lower limit of detection, shorter response time, and better accuracy and selectivity (Samardžić et al., 2017).

To the best of our knowledge, there are only two articles focused on determination of TBZ using direct potentiometry. Due to that fact, the aim of this work was to develop a new potentiometric sensor for TBZ determination, based on ionic pair of TBZ and 5-sulfosalicylate (TBZ-SAL) as sensor material, and to investigate the influence of variation of membrane components on the sensor response characteristics. The new sensor was characterized using direct potentiometry, and its applicability for TBZ determination in fruit samples was demonstrated using the Gran method.

2. Material and methods

2.1. Reagents and materials

TBZ (Acros Organics, Belgium) and HCl (Carlo Erba, Italy) were used to prepare the analyte. The newly prepared ionic pair of TBZ and 5-sulfosalicylic acid (SAL, Reanal, Hungary), tetrahydrofuran (THF, Fisher Scientific, UK), poly(vinyl chloride) (PVC, Fluka, Switzerland), *o*-nitrophenyl octyl ether (*o*-NPOE, Fluka, Switzerland), bis(2-ethylhexyl) sebacate (BEHS, Fluka, Switzerland), dibutyl phthalate (DBP, Fluka, Switzerland), 2-nitrophenyl phenyl ether (NPPE, Fluka, Switzerland), dibutyl sebacate (DS, Fluka, Switzerland), and bis(2-ethylhexyl) phthalate (DOP) were used for liquid membrane preparation. Lemons, oranges, and bananas used as real samples were purchased from the local store in Osijek (Croatia). Bananas originated from Ecuador and lemons and oranges from Spain. The fruit was not declared as bio. All salt solutions, L(+)-ascorbic acid (GRAM-MOL, Croatia), citric acid (GRAM-MOL, Croatia), glucose (Kemika, Croatia), fructose (Kemika, Croatia), imazalil (Sigma Aldrich, USA), and 2-phenylphenol (Sigma Aldrich, USA) were prepared using analytical grade chemicals, and all solutions were prepared using deionized water with a conductivity of 0.055 μS/cm.

2.2. Apparatus

An ultrasonic bath (BADELIN RK-100, Germany) was used for the preparation of the sensor membrane. The Thermo Nicolet Avatar 380 FTIR with Smart Orbit Diamond ATR (Thermo Scientific, USA) was used for ATR-FTIR spectra recording. The 794 Basic Titrino, 806 Exchange unit, 826 mobile pH meter, 728 stirrer, Tiamo software (all from Metrohm, Switzerland), and in-house software were used for measurements.

2.3. Preparation of the sensor

For preparation of the TBZ-SAL ionic pair, concentrated sulfuric acid was added dropwise to the aqueous suspension of TBZ, during vigorous stirring, until it became homogeneous, indicating that all of the solid material dissolved due to the protonation. Next, a concentrated aqueous solution of 5-sulfosalicylic acid was prepared and added to the solution of TBZ, followed by the formation of a white precipitate, which was the scarcely soluble ionic pair of protonated TBZ and 5-sulfosalicylate. The solid material was washed with plenty of deionized water to remove the excess of sulfuric and 5-sulfosalicylic acids by filtrating through a commonly used filtration paper. Finally, it was dried at room temperature.

For the preparation of the sensor membrane, the newly prepared sensor material, TBZ-SAL (0.00184 g, 1% w/w; 0.005442 g, 3% or 0.00907 g, 5%), PVC (0.05986 g, 33.0% w/w; 0.05859 g, 32.3% or 0.05750 g, 31.7%), plasticizer (*o*-NPOE (115 μL, 66.0% w/w), BEHS (131 μL, 66.0% w/w), DBP (115 μL, 66.0% w/w), NPPE (97 μL, 66.0% w/w), DS (128 μL, 66.0% w/w; 125 μL, 64.6% w/w; 123 μL, 63.3% w/w), and DOP (122 μL, 66.0% w/w)) were dissolved in 2 mL of THF using an ultrasonic bath. A glass ring fixed on a glass plate was used as a mold for the membrane mixture. After evaporation of the solvent (approximately 24 h), small membrane disks were excised and mounted on a Philips electrode body IS-561 (Glasblaeserei Moeller, Zurich, Switzerland). Sodium chloride ($c = 3$ M) was used as the internal filling solution of the sensor.

2.4. Procedure

Every day, before measurements, the sensor was conditioned in TBZ solution ($c = 1.0{\cdot}10^{-4}$ M) for 15 min and short calibration (concentration range between $1.0{\cdot}10^{-6}$ M and $1.0{\cdot}10^{-3}$ M) was performed to check performance of the sensor. All measurements were performed at room temperature, without ionic strength adjustments, using a new TBZ-SAL sensor as the working electrode and a silver/silver chloride electrode, with KCl ($c = 3$ M) as an inner electrolyte (Metrohm, Switzerland), as the reference. All analyte solutions were magnetically stirred and the pH was adjusted to 2.6. The solution volumes were 20 mL and 15 mL for response measurements and real sample analysis, respectively.

Response measurements were performed using TBZ solution ($c = 2.0{\bullet}10^{-3}$ M and $5.0{\bullet}10^{-5}$ M) incrementally added to distilled water using in-house software. The fixed interference method (Buck & Lindner, 1994) was used for measuring the influence of 15 potential interferences ($c = 1.0{\bullet}10^{-2}$ M for all but imazalil and 2-phenylphenol ($c = 2.5{\bullet}10^{-4}$ M)). For the influence of pH on the potentiometric response measurements, the pH was adjusted using NaOH and HCl solutions ($c =$ 1.0 M, $1.0{\cdot}10^{-1}$ M, and $1.0{\cdot}10^{-2}$ M) in the pH range between 2 and 8.

Real samples were prepared using peel of oranges, lemons, and bananas ($m = 100$ g). Chopped peel was placed in a glass and covered with distilled water ($V = 155$ mL, 151 mL, and 300 mL, respectively). The pH was adjusted, and after 24 h, the samples were filtered through the gauze and measurements were performed.

Between measurements, the new TBZ-SAL sensor was stored in deionized water. Thus, analytical characteristics were constant for approximately one month.

3. Results and discussion

3.1. ATR-FTIR characterization of TBZ-SAL

The formation of TBZ-SAL ionic pair, used as a sensor material in new TBZ-SAL sensor, was confirmed using ATR-FTIR characterization.

3.1.1. Thiabendazole

The following valence vibrations can be identified in the ATR-FTIR spectrum of TBZ (Fig. S2a). At 903 cm^{-1}, the symmetrical valence vibration characteristic of the C═C double bonds in the benzene ring of the imidazole appears, and at the value of 1,403 cm^{-1}, the asymmetric valence vibration characteristic of the C═C double bonds appears. There are also three vibrations characteristic of five-membered sulfur-containing heterocyclic rings: the valence vibration of the S—H bond at 1,094 cm^{-1}, the valence vibration of S═C of aromatic rings at 1,304 cm^{-1}, and the asymmetric valence vibration of = CH at 3,097 cm^{-1}. A low-intensity, flattening and elongated band appears in the wavenumber range of 2,300–3,200 cm^{-1}, indicating the presence of N—H valence vibrations in the benzdimidazole derivatives.

3.1.2. 5-sulfosalicylic acid

The spectrum of 5-sulfosalicylic acid (Fig. S2b) shows all the valence vibrations characteristic for the molecule. At 662 cm^{-1}, the valence vibration C═C characteristic for the aromatic ring can be identified in the fingerprint range. At 1,026 cm^{-1}, the valence vibration of the OH group attached to the phenol ring appears. The asymmetric valence vibration characteristic for the carboxyl group appears at a wavenumber of 1,118 cm^{-1}. In the case where there is no interaction between the carboxyl groups (intramolecular or intermolecular), the C═O and C-OH valence vibrations characteristic for the functional group appear together. In the case of 5-sulfosalicylic acid, these two peaks can be identified at 1,613 and 1,673 cm^{-1}. The intensity of the valence vibration of the sulfo-group is low in the case of solid-phase ATR-FTIR, but it can be clearly identified at 1,212 cm^{-1}. Between 2,732 cm^{-1} and 3,744 cm^{-1}, a moderately intense, elongated band is the valence vibration characteristic for hydroxyl groups.

3.1.3. TBZ-SAL complex

The ATR-FTIR spectra of the complex of TBZ and 5-sulfosalicylic acid (Fig. S2c) also show the valence vibrations identified above. In addition, two new vibrations can also be observed. For sulfone-functional compounds, when the sulfone group is involved in salt formation, a slightly broader, slightly wider peak is observed at 1,900–1,950 cm^{-1} (Varghese et al., 2007). This can also be identified for this complex compound at 1,942 cm^{-1}. Furthermore, between 3,297–3,604 cm^{-1}, a low-intensity doublet peak is observed, which is a valence vibration characteristic of protonated amine salts.

3.2. Response of the TBZ-SAL sensor

The membrane of the new TBZ-SAL sensor, which is responsible for its analytical characteristics, is based on ionic pair TBZ-SAL, formed according to Eq. (1):

$$TBZ^{+} + SAL^{-} \rightleftarrows TBZ - SAL \quad (1)$$

The solubility product constant for the formed ionic pair is:

$$K_{sp} = a_{TBZ^{+}} \bullet a_{SAL^{-}} \quad (2)$$

where $a_{TBZ^{+}}$ and $a_{SAL^{-}}$ are the activities of TBZ cation and SAL anion, respectively.

Due to its solubility in organic solvents and insolubility in water, TBZ-SAL can be used as a sensor material in TBZ-selective sensors which respond to TBZ according to the Nernst equation:

$$E = E^{0} + S \bullet log a_{TBZ^{+}} \quad (3)$$

where E = electrode potential, E^{0} = standard electrode potential, and S = sensor slope, which for TBZ cation amounts to 59.2 mV/decade of activity at 25 °C.

This TBZ-selective sensor can be easily used for simple determination of TBZ using direct potentiometry.

3.3. Optimization of the membrane composition

3.3.1. Selection of the plasticizer

Although the sensor material is the main component in the PVC-membrane of the sensor, the plasticizer, as the predominant element, improves flexibility of the membrane and represents the solvent for the ionophore, thus enhancing mobility inside the membrane (Zahran et al., 2014). Also, it is shown that the nature of the plasticizer has an influence on analytical performances (Nernstian response, limit of detection (LOD), selectivity) of PVC-membrane sensors (Bedlechowicz et al., 2002; Zahran et al., 2010). Considering the above, the influence of six plasticizers (*o*-NPOE, BEHS, DBP, NPPE, DS, and DOP) on the response characteristics of the new TBZ-SAL sensor was investigated. The weight ratio of PVC and plasticizer was 1:2 and the sensor material content was 1% in all sensors investigated, as is typical (Pechenkina & Mikhelson, 2015). TBZ solution was used for the investigation of the response characteristics of the TBZ-SAL sensor in a concentration range between $2.5 \bullet 10^{-8}$ M and $1.0 \bullet 10^{-3}$ M. The resulting responses and their statistics obtained using linear regression analysis are presented in Fig. 1a and Table 1. IUPAC recommendations (Umezawa et al., 2000) were used for LOD estimation. It can be seen that sensors with all plasticizers investigated, except DS, revealed a sub-Nernstian response. The sensor with NPPE exhibited the lowest slope value (32.5 mV/decade of activity), while the sensor with DS as plasticizer revealed a slope closest to Nernstian (62.2 mV/decade of activity). The useful concentration range was the same for all sensors investigated ($1.2 \bullet 10^{-6}$–$1.0 \bullet 10^{-3}$ M) except for sensor with DS as plasticizer ($8.6 \bullet 10^{-7}$–$1.0 \bullet 10^{-3}$ M). The lowest LOD exhibited sensors with BEHS and DBP ($1.3 \bullet 10^{-7}$ M and $2.5 \bullet 10^{-7}$ M, respectively), but their slope values were sub-Nernstian. Due to the best response characteristics, DS was chosen as the plasticizer for further investigation. The statistics was based on five repeated meaurements. The reproducibility of measuring responses to TBZ using the TBZ-SAL sensor with DS as plasticizer and 1% of sensor material can be seen in Figure S3. The reproducibility was excellent for all measurements performed, but for the clarity, all figures display one representative response.

3.3.2. Optimization of the sensor material content

To investigate the influence of sensor material content in the PVC-membrane, response characteristics obtained using three sensors with different content of sensor material (1%, 3%, and 5%) were compared. The weight ratio of PVC and plasticizer was the same in all investigations (1:2). The compositions of all membranes investigated are presented in Table S1. The comparison of the results is presented in Fig. 1b and Table S2. The best response characteristics (slope closest to Nernstian [62.2 mV/decade of activity] and LOD $3.2 \bullet 10^{-7}$ M) were revealed using membrane 1 with 1% of TBZ-SAL. Sensors with a higher percentage of sensor material revealed sub-Nernstian response and higher LOD, so membrane 1 was chosen for further investigation.

3.4. Dynamic response measurements

Dynamic response time is the time taken for the sensor to achieve 90% of the final potential value after an abrupt increase of TBZ concentration (Maccà, 2004). The dynamic response time measurement for the new TBZ-SAL sensor is presented in Fig. 2. The average response time was 8 s, which indicates a fast response of the new TBZ-SAL sensor.

3.5. Signal drift and life time of the new TBZ-SAL sensor

Sensor drift is fluctuation of the sensor potential over time caused by electronics stabilizing, temperature, etc. It was measured in TBZ solution ($c = 2.0 \cdot 10^{-3}$ M) at 25 °C using linear regression analysis, where drift represented the slope of the calculated linear regression line. For the new TBZ-SAL sensor, the signal drift was defined by the equation E (mV) = 0.00204·t(s) – 113.39 and amounted to ± 3.5 mV/hour

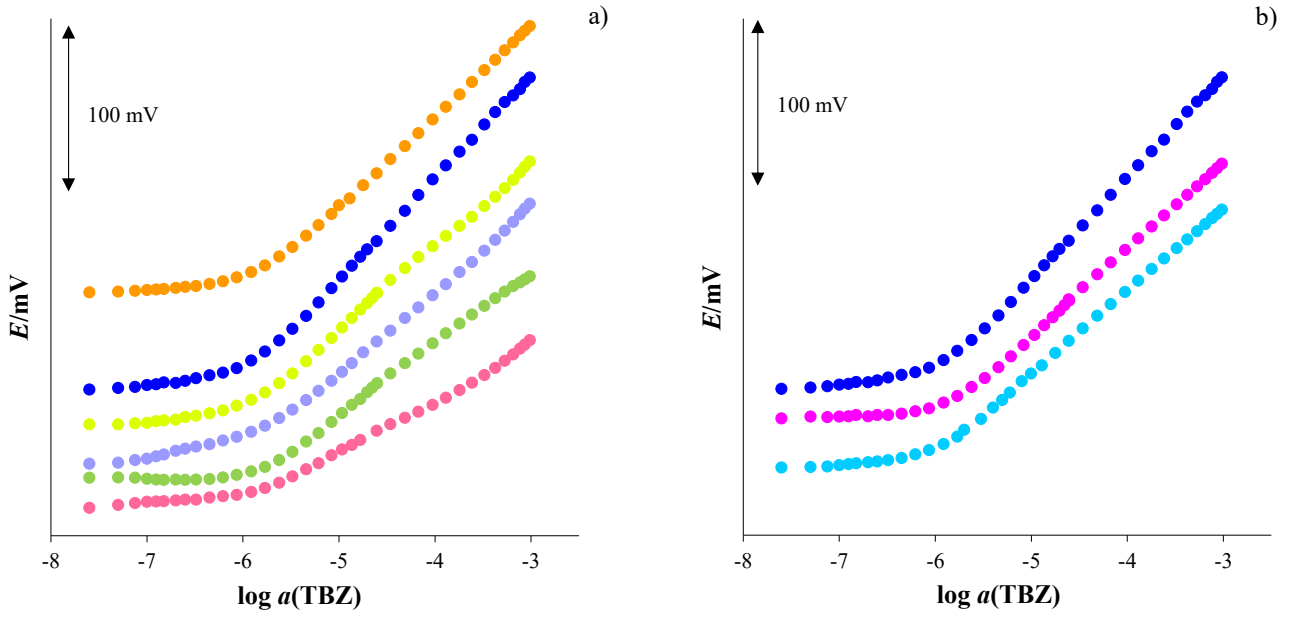

Fig. 1. Responses to TBZ obtained using the TBZ-SAL sensors with: a) different plasticizers (● *o*-NPOE, ● DS, ● DBP, ● BEHS, ● DOP and ● NPPE), b) different content of sensor material (● 1%, ● 3% and ● 5%). Here and in further figures, some curves are displaced laterally and/or vertically for clarity.

Table 1
Statistics of the response characteristics of TBZ-SAL sensors with different plasticizers to TBZ[a)].

Plasticizer	Slope [mV/ decade of activity]	Standard error	Correl. coeff. [R^2]	LOD [M]	Useful conc. range [M]
o-NPOE	55.0 ± 0.8	1.6	0.9990	$6.2•10^{-7}$	$1.2•10^{-6}$–$1.0•10^{-3}$
BEHS	50.5 ± 1.1	2.2	0.9978	$1.3•10^{-7}$	$1.2•10^{-6}$–$1.0•10^{-3}$
DBP	51.6 ± 0.8	1.7	0.9986	$2.5•10^{-7}$	$1.2•10^{-6}$–$1.0•10^{-3}$
NPPE	32.5 ± 1.0	2.0	0.9956	$6.2•10^{-7}$	$1.2•10^{-6}$–$1.0•10^{-3}$
DS	62.2 ± 0.9	1.7	0.9990	$3.2•10^{-7}$	$8.6•10^{-7}$–$1.0•10^{-3}$
DOP	44.1 ± 0.6	1.3	0.9989	$8.6•10^{-7}$	$1.2•10^{-6}$–$1.0•10^{-3}$

a) average of 5 determinations ± confidence limits (p = 0.95).

(Fig. S4).

The life time of the sensor represents a period of time in which the sensor can be used without significant changes in response characteristics. For the new TBZ-SAL sensor, the life time was approximately one month with daily measurements. It was checked performing a short calibration every day before measurements. After approximately one month of continuous use the calibration curve changed and the slope value of the TBZ-SAL sensor decreased (Fig. S5). The probable cause for such results is the leaching of the sensor material from the membrane, which is known as one of the main disadvantages of ISEs. Other possible reason could be the coextraction of other ions from the real sample solutions into the membrane of the sensor.

3.6. The influence of pH

The influence of pH on the response of the new TBZ-SAL sensor was investigated in a solution of TBZ ($c = 2.0·10^{-3}$ M) in the pH range between 2 and 8. It can be seen in Fig. S6 that the potential was stable in the pH range between 2 and 4. At higher pH values, an abrupt potential decrease was observed due to deprotonation of TBZ ion in the water phase, on the membrane surface. Considering the results, all measurements were performed at pH 2.6, which was also the optimal pH value for dissolving TBZ in water and its extraction from the fruit peel into the solution.

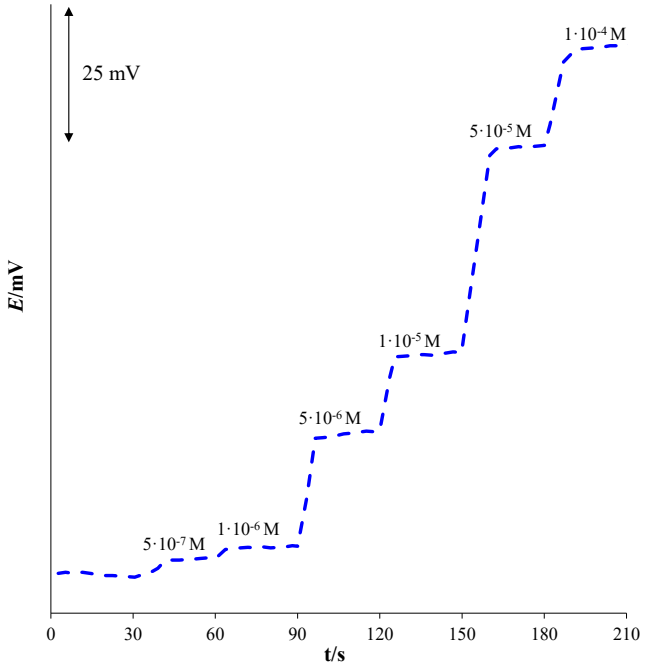

Fig. 2. Dynamic response of the TBZ-SAL sensor.

3.7. The selectivity investigation

The selectivity measurements were performed using the fixed interference method, where potential was measured in a solution with constant activity of interfering ion ($c = 1.0·10^{-2}$ M or $2.5·10^{-4}$ M) and TBZ concentration in range between $1.0·10^{-6}$ M and $1.0·10^{-3}$ M or

$2.5{\cdot}10^{-8}$ M and $2.5{\cdot}10^{-5}$ M, respectively. The Nikolskij-Eisenman equation was mathematically adjusted to experimental data, obtained using *Solver* (Microsoft Excel), in order to estimate the potentiometric selectivity coefficients:

$$E = E^{\circ} + \frac{2,303RT}{z_A F}\log\left[a_A + \sum_{B=1}^{N} K_{A,B}^{pot} a_B^{\frac{z_A}{z_B}}\right] \quad (4)$$

where $K_{A,B}^{pot}$ is the potentiometric selectivity coefficient, a_A and a_B are the activities and z_A and z_B are the charges of the analyte ion and the interfering ion, respectively.

The potentiometric selectivity coefficients indicate how many times the interferent activity can be higher than the TBZ activity while keeping the sensor potential the same. The resulting values are presented in Table 2. It can be seen that the new TBZ-SAL sensor has good selectivity for TBZ. Only imazalil and 2-phenylphenol exhibited interference.

3.8. Determination of TBZ in pure and real samples

The applicability of the new TBZ-SAL sensor to determine TBZ was tested in pure and real systems. As pure systems, five TBZ solutions were used ($c = 3.0{\cdot}10^{-4}$ M, $1.0{\cdot}10^{-4}$ M, $3.5{\cdot}10^{-5}$ M, $1.0{\cdot}10^{-5}$ M, and $3.0{\cdot}10^{-6}$ M) and as real systems, fruits (lemons, oranges, and bananas) purchased from the local store were used. Lemons, oranges, and bananas were chosen for this investigation because TBZ is a component of waxes applied on citrus fruit, and is commonly used for treatment of bananas in order to ensure their freshness. To prepare testing solutions, 100 g of chopped peel was placed in a glass and covered with distilled water, the pH was adjusted to 2.6, and after 24 h, the samples were filtered and measurements were performed.

Pure systems were analysed using direct potentiometry and the Gran method in order to check the accuracy of TBZ determination using the new TBZ-SAL sensor. In direct potentiometric measurements, potential was measured in TBZ solution; according to the calibration graph (voltage against log of activity) and the equation of a line, the TBZ concentration was calculated. For the Gran method, as extension of the standard addition method, 13 standard additions (TBZ solution, $c = 2.0{\cdot}10^{-3}$ M) were spiked in every solution and corresponding potentials were measured. That potential responds to TBZ according to Equation (5):

$$E = k + S \bullet \log c \quad (5)$$

where k = constant and c = TBZ concentration.

Eq. (6) follows from Eq. (5):

$$c = 10^{\frac{E-k}{S}} = \frac{10^{\frac{E}{S}}}{10^{\frac{k}{S}}} \quad (6)$$

The TBZ concentration after every standard addition can be calculated according to Eq. (7):

$$c = \frac{c_x V_0 + c_s V_s}{V_0 + V_s} \quad (7)$$

where c_x = TBZ concentration before standard addition, V_0 = volume of the solution before standard addition, c_s = concentration of the standard addition solution, and V_s = volume of the standard addition.

From Eq. (6) and Eq.7, Eq. (8) can be obtained:

$$\frac{c_x V_0 + c_s V_s}{V_0 + V_s} = 10^{\frac{E-k}{S}} \quad (8)$$

After rearrangement, it follows:

$$10^{\frac{E}{S}}(V_0 + V_s) = 10^{\frac{k}{S}} c_x V_0 + 10^{\frac{k}{S}} c_s V_s \quad (9)$$

After dividing the sensor response with the standard addition with those without addition, and after rearrangement, Eqs. (10) and (11) are obtained:

$$\frac{10^{\frac{E_1-k}{S}}(V_0 + V_s)}{10^{\frac{E_0-k}{S}} \bullet V_0} = \frac{c_x V_0 + c_s V_s}{c_x V_0} \quad (10)$$

$$10^{\frac{E_1-E_0}{S}}(V_0 + V_s) = V_0 + \frac{1}{c_x} c_s V_s \quad (11)$$

A plot of $10^{\frac{E_1-E_0}{S}}(V_0 + V_s)$ against $c_s V_s$ results with straight line graph, with a negative intercept that represents the negative amount of TBZ in the sample before standard additions. Considering the volume of the sample, the TBZ concentration in samples can easily be calculated. The comparison of the results for TBZ determination in pure systems (TBZ solutions of known concentration) using the new TBZ-SAL sensor obtained using direct potentiometry and the Gran method are presented in Table 3. Considering low concentrations of the samples and that direct potentiometry is known as a method that can be easily influenced with various factors, the results obtained using both methods are acceptable. However, the slightly better results were obtained using the Gran method, which was expected considering that the Gran method is based on multiple standard additions. Higher deviation from the accuracy was occurred in solutions with lower TBZ concentrations, which was also expected. Due to the results, the Gran method was chosen for TBZ determination in real samples (fruit peel).

After confirming the accuracy of the TBZ-SAL sensor, the TBZ concentration was determined in the peels of lemons, oranges, and bananas using the Gran method described above. The known addition of TBZ ($c = 2.0{\cdot}10^{-3}$ M) was used to investigate the matrix component interference, and accuracy of the TBZ determination. The results of these measurements are presented in Table 4. The results confirm the accurate TBZ determination in the complex matrix. Although the TBZ can be found in real samples in wide range of concentrations, the TBZ

Table 2
Potentiometric selectivity coefficients of new TBZ-SAL sensor obtained by fixed interference method.

Interference	$pK_{A,B}^{pot}$
Ammonium	3.67
Sodium	3.93
Calcium	4.85
Magnesium	5.48
Ascorbic acid	4.42
Citric acid	2.66
Potassium	3.12
Copper	2.91
Zinc	4.09
Lithium	3.73
Iron (III)	3.56
Glucose	3.62
Fructose	3.63
Imazalil	0.82
2-phenylphenol	1.67

Table 3
Results of the TBZ determination in the pure systems (TBZ solutions) obtained using direct potentiometry and the Gran method and TBZ-SAL sensor[a)].

TBZ added [M]	TBZ found [M]		Recovery [%]	
	Direct potentiometry	Gran method	Direct potentiometry	Gran method
$3.00{\cdot}10^{-4}$	$3.39{\cdot}10^{-4}$	$3.26{\cdot}10^{-4}$	113.0	108.7
$1.00{\cdot}10^{-4}$	$1.15{\cdot}10^{-4}$	$1.05{\cdot}10^{-4}$	115.0	105.0
$3.50{\cdot}10^{-5}$	$3.81{\cdot}10^{-5}$	$3.54{\cdot}10^{-5}$	108.9	101.1
$1.00{\cdot}10^{-5}$	$1.22{\cdot}10^{-5}$	$1.13{\cdot}10^{-5}$	122.0	113.0
$3.00{\cdot}10^{-6}$	$2.34{\cdot}10^{-6}$	$2.42{\cdot}10^{-6}$	78.0	80.7

[a)]average of 3 determinations.

Table 4
Results of the TBZ determination in the real systems (fruit peel) obtained using Gran method and TBZ-SAL sensor[a)].

Sample	TBZ found [M]	TBZ found [mg/g of the peel]	TBZ added [mol]	TBZ found [mol]	Recovery [%]
Orange	$2.69{\cdot}10^{-4}$	0.084	$1.00{\cdot}10^{-5}$	$1.05{\cdot}10^{-5}$	105.3
Lemon	$1.29{\cdot}10^{-4}$	0.039	$1.00{\cdot}10^{-5}$	$1.02{\cdot}10^{-5}$	102.4
Banana	$7.33{\cdot}10^{-5}$	0.044	$1.00{\cdot}10^{-5}$	$1.07{\cdot}10^{-5}$	107.0

a) average of 3 determinations.

concentrations determined in fruit purchased from the local stores using the new TBZ-SAL sensor are comparable with results demonstrated in other publications (Blazheyevskiy et al., 2016; Rosenblum & Meriwether, 1970). The typical example of Gran plot obtained measuring TBZ in orange peel is demonstrated in Fig. S7.

4. Conclusion

TBZ-SAL sensors with six different plasticizers and various content of the sensor material in the membrane were prepared and compared. The sensor containing DS as plasticizer and 1% sensor material showed the best characteristics and was chosen for further investigations. It had a working range between $8.6{\bullet}10^{-7}$–$1.0{\bullet}10^{-3}$ M with a Nernstian slope (62.2 mV/decade of activity). The response time of the sensor was only 8 s, it had a pH working range between 2 and 4, and good selectivity toward TBZ. The life time of the new sensor was approximately one month with daily measurements. All of these parameters lead to applicability of the TBZ-SAL sensor for TBZ determination in real samples (peel of oranges, lemons, and bananas). The accuracy of the sensor was tested by comparison of the results for TBZ determination in TBZ solutions of known concentration using the new TBZ-SAL sensor, obtained using direct potentiometry and the Gran method. Considering better results were obtained using the Gran method, it was chosen for TBZ determination in real samples.

CRediT authorship contribution statement

Mateja Budetić: Conceptualization, Methodology, Validation, Investigation, Writing – original draft, Writing – review & editing, Visualization, Supervision. **Mirela Samardžić:** Conceptualization, Methodology, Validation, Investigation, Writing – original draft, Writing – review & editing, Visualization, Supervision. **Karlo Bubnjar:** Resources, Investigation. **Andrea Dandić:** Resources. **Pavo Živković:** Resources. **Aleksandar Széchenyi:** Investigation, Writing – original draft, Writing – review & editing, Funding acquisition. **László Kiss:** Conceptualization, Investigation, Writing – original draft, Writing – review & editing.

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.

Acknowledgements

This study is supported by the European Structural and Investment Funds grant for the Croatian National Scientific Center of Excellence for Personalized Health Care, Josip Juraj Strossmayer University of Osijek (grant #KK.01.1.1.01.0010). The research in Hungary was funded by NKFIH (NKFI-137793) and within the framework of the University of Pécs' project TKP2021-EGA-17.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodchem.2022.133290.

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