Coefficient of diffusion of tannins in extracts from red and black hawthorn fruit

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Abstract. One of the main parameters of the extraction process is the coefficient of diffusion. It gives information about the diffusion properties of the material to be extracted and depends on various factors: raw material structure, solvent type, temperature, process duration, etc. Determination of molecular diffusion coefficients in extraction from red (*Crataegus monogyna* Jacq.) and black (*Crataegus nigra* Waldst & Kit) hawthorn is an objective of the work. The extracts were obtained by ultrasonic extraction with 50 and 70% ethanol at three temperatures (20, 40 and 60°C). The highest values of coefficients for both hawthorn species were obtained at 60°C with 50% ethanol – $5.13.10^{-6}$ m^2/s for black hawthorn and $6.4.10^{-6}$ m^2/s for red hawthorn.

1 Introduction

Ultrasonic extraction is an innovative and efficient method for extracting biologically active substances from plant materials.

Ultrasonic extraction uses the energy from an ultrasonic wave. Ultrasound accelerates the processes of dissolution of the bioactive substances in the solvent and their transport (diffusion), thus improving the extraction. The other presentation of ultrasonic extraction is the reduced consumption of solvents and energy, lower temperature treatment of the raw plant materials during extraction, thus preserving the bioactive substances to a high degree [1, 2].

An important parameter of the process of substance transfer during the extraction, is the coefficient of diffusion. Its value depends on the factors, including the nature of the solvent, temperature, pressure, plant tissue structure, *etc*. [3].

The driving force in this process is the concentration gradient of solutes. The diffusion behaviour of the raw material, respectively of the biologically active substances treated with ultrasonic waves is an important parameter in order to understand the mass transfer behaviour of the process. The diffusive properties of the extractable material is the coefficient of diffusion, which is different depending on the raw plant materials used [4].

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Red hawthorn (*Crataegus monogyna* Jacq.) and black hawthorn (*Crataegus nigra* Waldst & Kit) belong to the family Rosaceae and are common plants. In our country they grow up to 1500 m altitude, the first species being the most widespread. Their fruits are mainly used in folk medicine [5].

Species of the genus *Crataegus* are a rich source of biologically active substances [5,6]. The fruits, leaves and flowers of hawthorn contain flavonoids, tannins, *etc*. [7-9].

There is no data in the literature on the determination of the content of tannins and coefficient of diffusion in the extraction of red and black hawthorn fruits by ultrasound, which is the aim of the present study. The obtained data will enrich the scientific research on different hawthorn species, which will extend their range of application – in the food industry, cosmetics, and pharmaceutics.

2 Materials and methods

2.1 Plant material

Berries of red (*Crataegus monogyna* Jacq.) and black (*Crataegus nigra* Waldst & Kit) hawthorn purchased from the commercial network were used. The hawthorn fruits were hand-picked and air-dried at room temperature (22°C), then stored in tightly closed plastic bags at a temperature of 5-8°C until processing.

The moisture and tannin content of the fruits was determined [10].

2.2 Extraction of the fruits

An ultrasonic bath was used, model ELMA, Elmasonic P30H – Germany, set to 37 kHz frequency.

Extraction of dried hawthorn fruits was carried out in a batch static mode by maceration in the solvent under the following conditions: solvent – 50 and 70% ethanol; size of fruit particles from 0.002 to 0.003 m; ratio of raw material to solvent = 1:10; temperature – 20, 40 and 60°C; duration of extraction – 1 h. The solvent was fully replaced and analysed for extracted tannins every 10 min. The criteria for effectiveness of the process was the quantity of extracted tannins.

The coefficient of diffusion *(D_{int})* of tannins were determined for each 10 min [11]:

2.3 Statistical analysis

The experiments were provided in three repetitions.

3 Results and discussion

The content of the moisture of the analysed fruits was 11.5% (black hawthorn) and 12.3 % (red hawthorn). The tannins concentration was 1.3% (black hawthorn) and 2.5% (red hawthorn).

The extracts were graded according to their tannin content, and their variation (over 10 min for 1 h) is presented in Figs. 1-4. The data shows that their amount is highest during the first 10 min, regardless of other process parameters, and it decreases with each subsequent extraction.

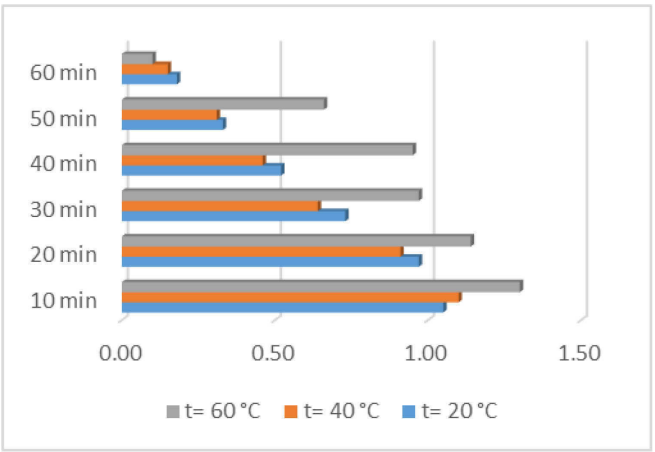

Fig. 1. Tannins in extracts from black hawthorn fruits with solvent 50% ethanol.

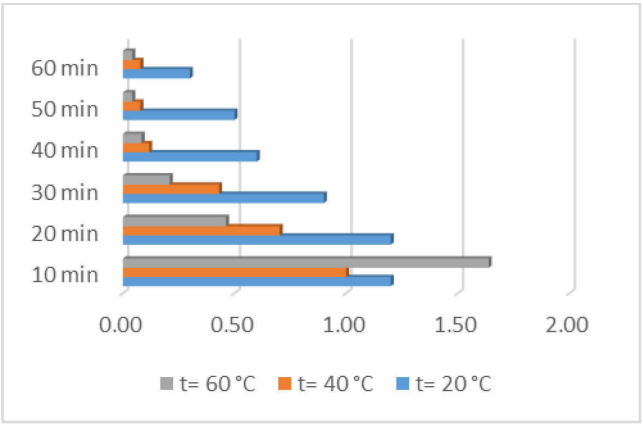

Fig. 2. Tannins in extracts from red hawthorn fruits with solvent 50% ethanol.

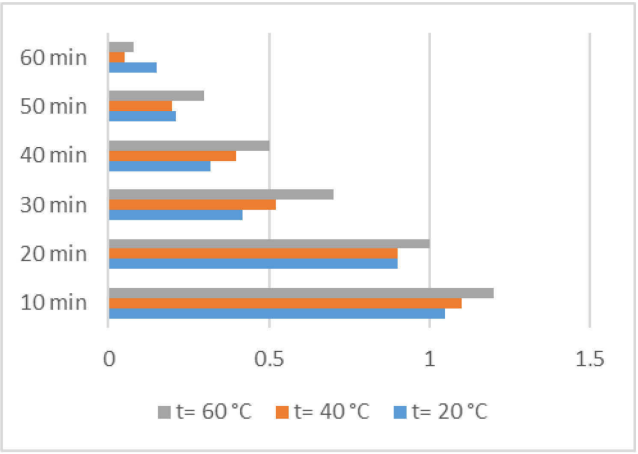

Fig. 3. Tannins in extracts from black hawthorn fruits with solvent 70% ethanol.

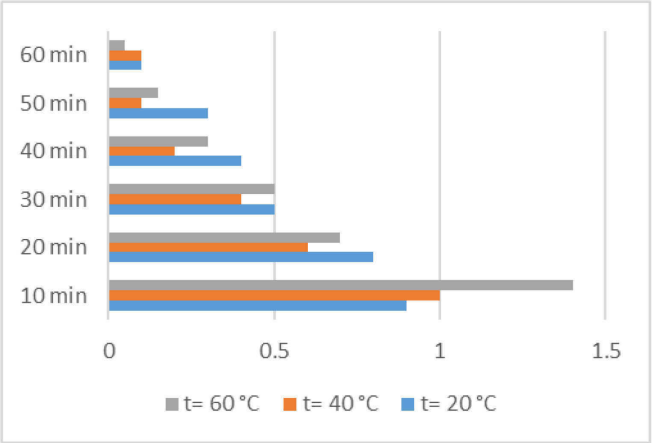

Fig. 4. Tannins in extracts from red hawthorn fruits with solvent 70% ethanol.

The obtained results prove the relationship between tannin yield with temperature and extraction duration. The concentration of tannins for each 10 min decreased with time. A similar dependence has been found for extraction of other raw materials [4, 12, 13].

Regardless of the type of hawthorn, the concentration of tannins was highest at 60°C, which is probably due to the relationship between the temperatures and the type of solvent. The variation in tannin concentrations throughout the determination period (60 min) for both hawthorn species were identical.

In the ultrasonic extraction of black hawthorn with 50% ethanol, the tannin content was highest (1.29%) at 60°C in the first 10 min, while in red hawthorn it was 1.64% Increasing the temperature from 20 to 60°C resulted in a gradual increase in tannin concentration in the first 10 min.

Similar results were obtained for extraction of common hawthorn but without the use of ultrasound, the concentration of extracted tannins being significantly less with the same technological parameters (0.4-0.6%) [11].

Based on these results, the coefficient of diffusion was calculated and its variation is presented in Figs. 5-8. Its values were highest for red hawthorn ($6.4.10^{-6}$ m^2/s) at the following process parameters – 50% ethanol, ratio between material and solvent = 1:10 and 60°C temperature.

In black hawthorn fruits (Figs. 5 and 6), the coefficient of diffusion has a different value ($5.13.10^{-6}$ m^2/s), even though the technological parameters are the same, explained by differences in species qualities [5].

As the temperature increases, so does the coefficient of diffusion values for both hawthorn species.

When extracted with 70% ethanol, the highest coefficient of diffusion values for black hawthorn were: with 70% ethanol – $4.4.10^{-6}$ m^2/s and for red hawthorn – $5.6.10^{-6}$ m^2/s. The minimal differences were observed.

From the analyses, it can be summarized that ultrasonic extraction improves the extraction process of biologically active substances from raw plant materials and reduces solvent consumption and extraction time.

The data obtained by us are different from those published in the literature for other plants [5]. This can be explained both by their different cellular structure and by different content of biologically active substances and the technological parameters of the extraction,

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The data obtained allow to make a summary that in ultrasonic extraction the extraction of biologically active substances is in a shorter time and at a lower solvent consumption,

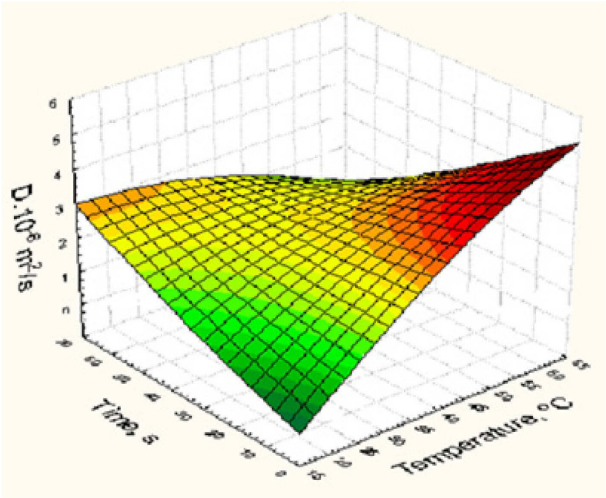

Fig. 5. Extracts from black hawthorn fruits with solvent 50% ethanol.

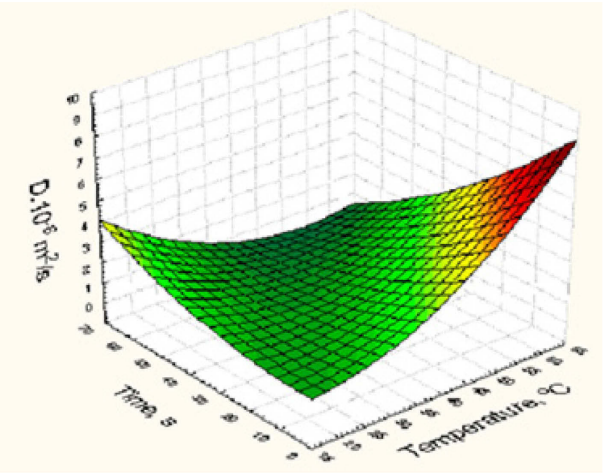

Fig. 6. Extracts from red hawthorn fruits with solvent 50% ethanol.

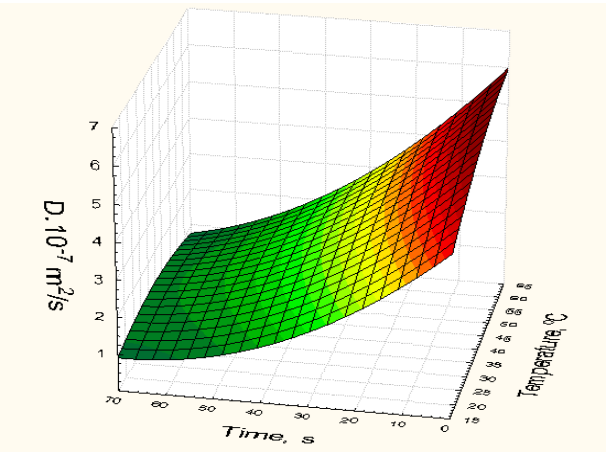

Fig. 7. Extracts from black hawthorn fruits with solvent 70% ethanol.

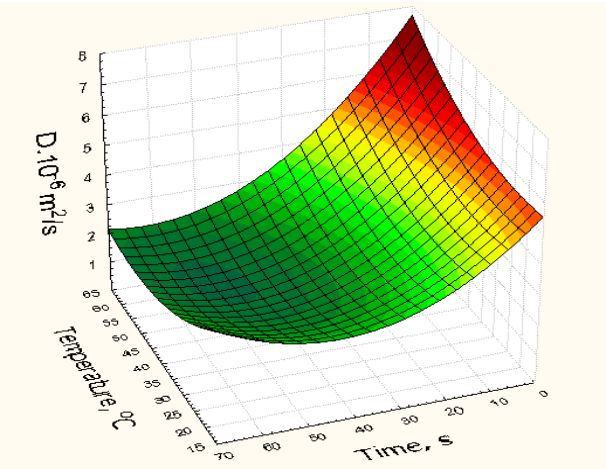

Fig. 8. Extracts from red hawthorn fruits with solvent 70% ethanol.

4 Conclusion

For the first time, ultrasonic extraction with ethanol with concentrations of 50 and 70% was carried out to determine the molecular diffusion coefficient.

The highest values of coefficient of diffusion for the two hawthorn species were obtained at 60°C with 50% ethanol – $5.13.10^{-6}$ m^2/s for black and $6.4.10^{-6}$ m^2/s for red hawthorn.

The results of the study can be used for further investigation of hawthorn species growing in Bulgaria in order to reveal their bioactivity, benefits and potential for application in the food products.

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