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OPTIMIZATION OF THE COMPOSITION OF THE EXTRACTANT MIXTURE FOR THE EXTRACTION OF NATURAL ORGANIC COMPOUNDS FROM PROCESSING PRODUCTS OF VEGETABLE RAW MATERIALS AND THEIR FURTHER USE IN THE PRACTICE OF ANTI-CORROSION PROTECTION

ОПТИМІЗАЦІЯ СКЛАДУ РОЗЧИНННИКА ДЛЯ ЕКСТРАКЦІЇ ПРИРОДНИХ ОРГАНІЧНИХ СПОЛУК ІЗ ПРОДУКТІВ ПЕРЕРОБКИ РОСЛИННОЇ СИРОВИНИ ДЛЯ ПОДАЛЬШОГО ЇХ ВИКОРИСТАННЯ В ПРАКТИЦІ АНТИКОРОЗІЙНОГО ЗАХИСТУ

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ABSTRACT

Purpose. To theoretically substantiate and experimentally confirm the conceptual approach to the use of the *i*-PrOH-EtOH-H_2O extractant system for obtaining plant extracts of grape, apricot, peach and tomato pomace with multifunctional anti-corrosion purposes.

Methodology. The optimization of the three-component composition of the extractant system was carried out by the Scheffe simplex grid planning method with the construction of concentration triangles, the quantitative content of the sum of phenolic compounds, the total content of flavonoids, and the sum of volatile compounds was used as a response function, and the "composition-anticorrosion efficiency" dependence was established in neutral water and air environments.

Scientific novelty. Use of the *i*-PrOH-EtOH-H_2O extractant system in the ratio of propanol - 50 ÷ 40 %; ethanol – 25 ÷ 30 %; water – 15 ÷ 25 % with a polarity index ~ 5.9 ÷ 6.3, is a criterion parameter for the extraction of substances that belong to different groups of natural organic compounds: plants secondary metabolism terpene and polyphenolic compounds.

Conclusions. It was established that the optimal use of the *i*-PrOH-EtOH-H_2O extractant system with a percentage ratio of solvents in the range of 50-40 %; 25 ÷ 30 %; 15 ÷ 25 %, respectively. The calculated polarity index is in the range of ~ 5.87 ÷ 6.37 and is a criterion parameter for the system of extractants relative to the studied raw materials. By comparing the areas of optima with the construction of simplex lattice plans where the inhibitory effect is selected as the response function, it was established that the criterion parameters of the component composition of the extracts for their use as multifunctional inhibitors are the total content of phenolic compounds at the level of ~90 ÷ ≥150 mg of the extract, flavonoids ~ 22 ÷ ≥56 mg of extract and 70 ÷≥ 96 mg of terpene compounds per 100 g of extract.

Key words: terpene and polyphenolic compounds. corrosion inhibitor, grape, apricot, peach, tomato cake

АНОТАЦІЯ

Мета роботи. Теоретично обґрунтувати та експериментально підтвердити концептуальний підхід до використання системи екстрагентів *i-PrOH-EtOH-*H_2O для отримання рослинних екстрактів жмиха винограду, абрикосу, персика та томату багатофункціонального протикорозійного призначення.

Методологія. Оптимізацію трикомпонентного складу системи екстрагенту проведено методом симплекс-градкового планування Шеффе з побудовою концентраційних трикутників, як функція відгуку використовували кількісний вміст суми фенольних сполук, загального вмісту флавоноїдів, та суми летких сполук та встановлення залежності “склад-протикорозійна ефективність” у нейтральних водних та повітряних середовищах.

Наукова новизна. Використання системи екстрагентів *i*-PrOH-EtOH-H_2O у співвідношенні у діапазоні пропанолу – 50 – 40 %; етанолу – 25 ÷ 30 %; води – 15-25 %. із індексом полярності ~ 5,9 – 6,3, є критеріальним параметром для забезпечує вилучення речовин, які належать до різних груп природніх органічних сполук: терпенових та поліфенольних сполук.

Висновки. Встановлено, що оптимальним є використання системи екстрагентів *i*-PrOH-*Et*OH-H_2O із відсотковим співвідношенням розчинників у діапазонах 50 – 40 %; 25-30 %; 15-25 %, відповідно. Розрахований індекс полярності знаходиться у межах ~ 5.87 – 6.37 і є критеріальним параметром для системи екстрагентів відносно досліджуваної сировини. Співставленням областей оптимумів із побудовою симплекс решітчастих планів де у якості функцій відгуку обрано ступінь захисту (інгібуючу дію, Z %) встановлено, що межевими параметрами компонентного складу екстрактів для їх використання як багатофункціональних інгібіторів є загальний вміст фенольних сполук на рівні ~ 90÷≥150 мг екстракту, флавоноїдів ~ 22÷≥56 мг екстракту та 70 ÷ ≥96 мг терпенових сполук на 100 г екстракту.

Ключові слова: терпенові та поліфенольні сполуки, інгібітор корозії, виноград, абрикос, персик, виноград, абрикос, персик, томат жом

Introduction

The problem of ensuring the reliable functioning of equipment/products operating/operated in aggressive corrosive environments, which is a condition for ensuring effective technological processes in various industries, is becoming more and more relevant both in Ukraine and around the world [1]. According to the EU strategy, regulations related to the use of toxic solvents, the constant increase in the price of raw materials, are a stimulating factor for the development of modern, environmentally safe anti-corrosion protection products, which are aimed at the economic development of society, and provide for the effective use of innovative, resource-saving "green" chemical technologies based on natural organic compounds of secondary natural resources [3-7]. Despite the rapid global development of research in the vector of obtaining "green" corrosion inhibitors based on plant raw materials, the absolute majority of them are directed to selective action in a certain corrosive environment, and the scientific basis of their production with systematic, scientifically based and generalized data, regarding the establishment of criterion parameters technologies for obtaining plant extracts, their influence on the component composition and protective effect, are almost absent. At the same time, waste from the food/plant industry is a source of a wide range of natural organic compounds [5]. The purposeful selection of a solvent/solvent system can provide multifunctionality of inhibitory protection in various corrosive environments, and the combination of plant extracts with additives - synergists to solve the classic problem of instability and briefly duration of their protective action, and become the basis for the development of new highly effective corrosion inhibitors of a wide spectrum of protective action for various purposes.

The most industrially demanded and at the same time scientifically unresolved and urgent issue is the development of multifunctional corrosion inhibitors with high efficiency of action in corrosive-aggressive water and air/atmospheric environments [5-7]. Purposeful creation of "green" corrosion inhibitors of this type should be based on extracting from plant raw materials a mixture of a wide range of substances belonging to different classes of organic compounds with different physicochemical properties. Therefore, *the aim* of the work was to justify the scientific principles of developing an optimal extractant/ system of extractants for obtaining multifunctional corrosion inhibitors based on its use.

Results of the research

The results of the research presented in the previous section indicate that in order to obtain extracts that would contain both terpenes and a wide list of polyphenolic compounds for further effective use in anti-corrosion protection, it is necessary to optimize the composition of the extractant mixture. Optimization of the composition of the three-component mixture for the studied types of plant raw materials was carried out by the simplex method (Scheffe simplex grid planning method) on the basis of preliminary experimental data for individual solvents (*i*-PrOH, EtOH, H_2O) and additional quantitative determination of the total content of phenolic compounds, flavonoids and GC-MS analysis content of terpene compounds. Ethanol (EtOH)(X1), 2-propanol (*i*-PrOH) (X2) and water (H_2O) (X3) were used as components for calculating simplexes. The corresponding simplex lattice plans were obtained for the optimization of the composition and the subsequent conduct of the experiment and obtaining extracts. The following parameters were selected as response functions: the total content of polyphenolic compounds, flavonoids, and the content of volatile compounds. Examination of the three-component systems shows that the contour plots show a rather limited optimized experimental field of the proportional mixture for the extraction of volatile compounds, while the optimum zone (optimal area) for the extraction of polyphenolic compounds and flavonoids was much wider (Fig. 1-2). Concentration triangles when optimizing the composition of the extractant of polyphenolic compounds indicates that the optimum zone is focused almost in the center of the triangle with a slight admixture to the region of the propanol/water binary mixture. The highest value of the total content of phenolic compounds is predicted to be at the level of 90-230 mg/100 g of extract in terms of Quercetin.

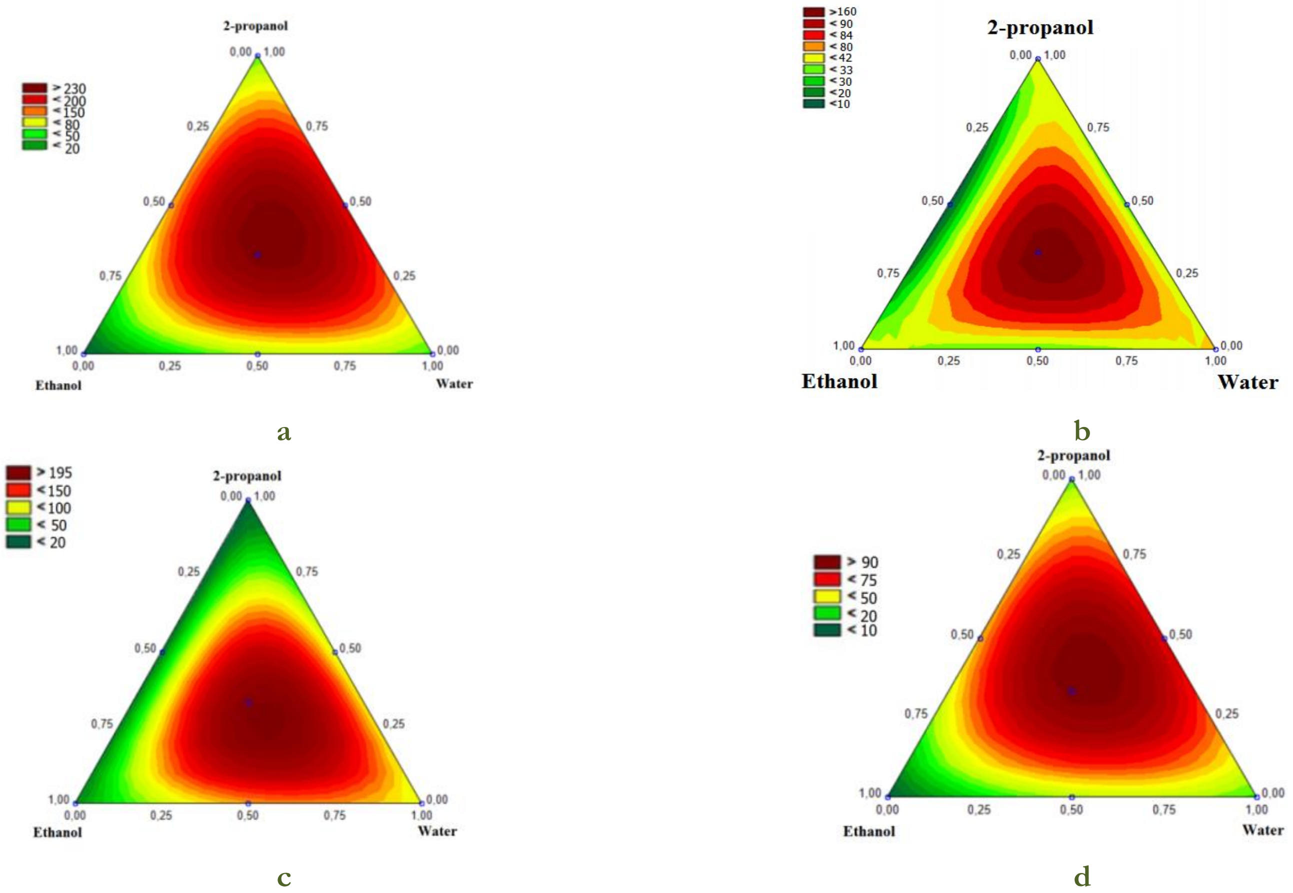

Fig.1. Dependencies of the total content of phenolic compounds on the composition of the extractant for grape cake (a), apricot (b), peach (c) and tomato (d)

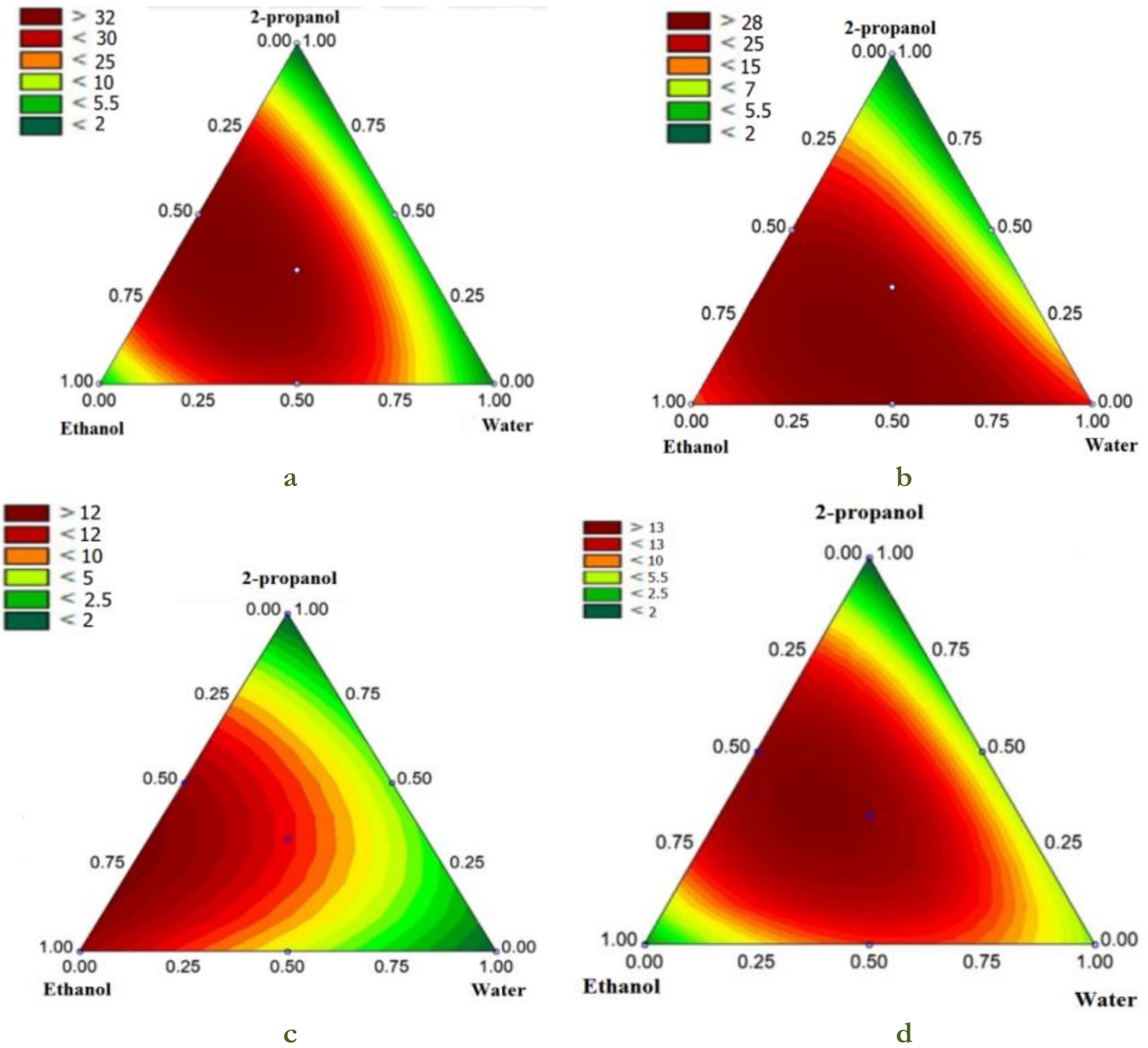

Fig. 2. Dependence of the total content of flavonoids on the composition of the extractant for grape cake (a), apricot (b), peach (c) and tomato (d)

In this way, summarizing the results of optimizing the composition of the extractant mixture according to the criterion parameters of the content of polyphenolic compounds [6], flavonoids and the content of volatile compounds and taking into account the purpose of extractant selection, which would collectively contribute to the extraction of a wide list of the above-mentioned classes of compounds, the *i*-PrOH-EtOH-H_2O extractant system in the ratio in the range of *i*-PrOH - 50 – 40 %; EtOH – 25 – 30 %; H_2O - 15-25% according to calculations based on experimental data is predicted to be the most optimal. Corresponding simplex lattice plans were built and implemented, where the inhibitory effect was chosen as the response function. Simplex analysis shows that the optimal composition of this mixture for the studied extracts is as follows: EtOH - 55 – 75 %; *i*-PrOH - 20-50 %; H_2O - 45 – 70 %.

The analysis of concentration triangles indicates that for the extraction of flavonoids for all studied types of plant raw materials, it is effective to use a mixture with a relatively high content of ethanol and water, the proportion of propane is less than a third (Fig. 2). The highest value of the total content of flavonoids is predicted to be at the level of 25-30 mg/100 g of extract in terms of gallic acid. The ratio of propanol/ethanol/water components, which is predicted to be effective for the extraction of flavonoids according to the calculated optimization results, is in the following ranges: EtOH – 65 – 77 %; *i*-PrOH - 20-30 %; H_2O - 55-80 %. It is natural that for the extraction of volatile compounds, the optimum zone is located almost at the top of the triangle, which indicates the effective use of propane in an almost predominant amount (Fig. 3). Depending on the type of plant material, the optimum zone shifts either to the binary mixture of *i*-PrOH-EtOH or *i*-PrOH - H_2O. Simplex analysis shows that the optimal composition of this mixture for the studied extracts is as follows: EtOH - 5 – 15 %; *i*-PrOH - 60 – 80 %; H_2O - 5 – 70 %. It is also quite obvious that the area of maximum antioxidant activity is located closer to the top of the ethanol side (Fig. 4) [7].

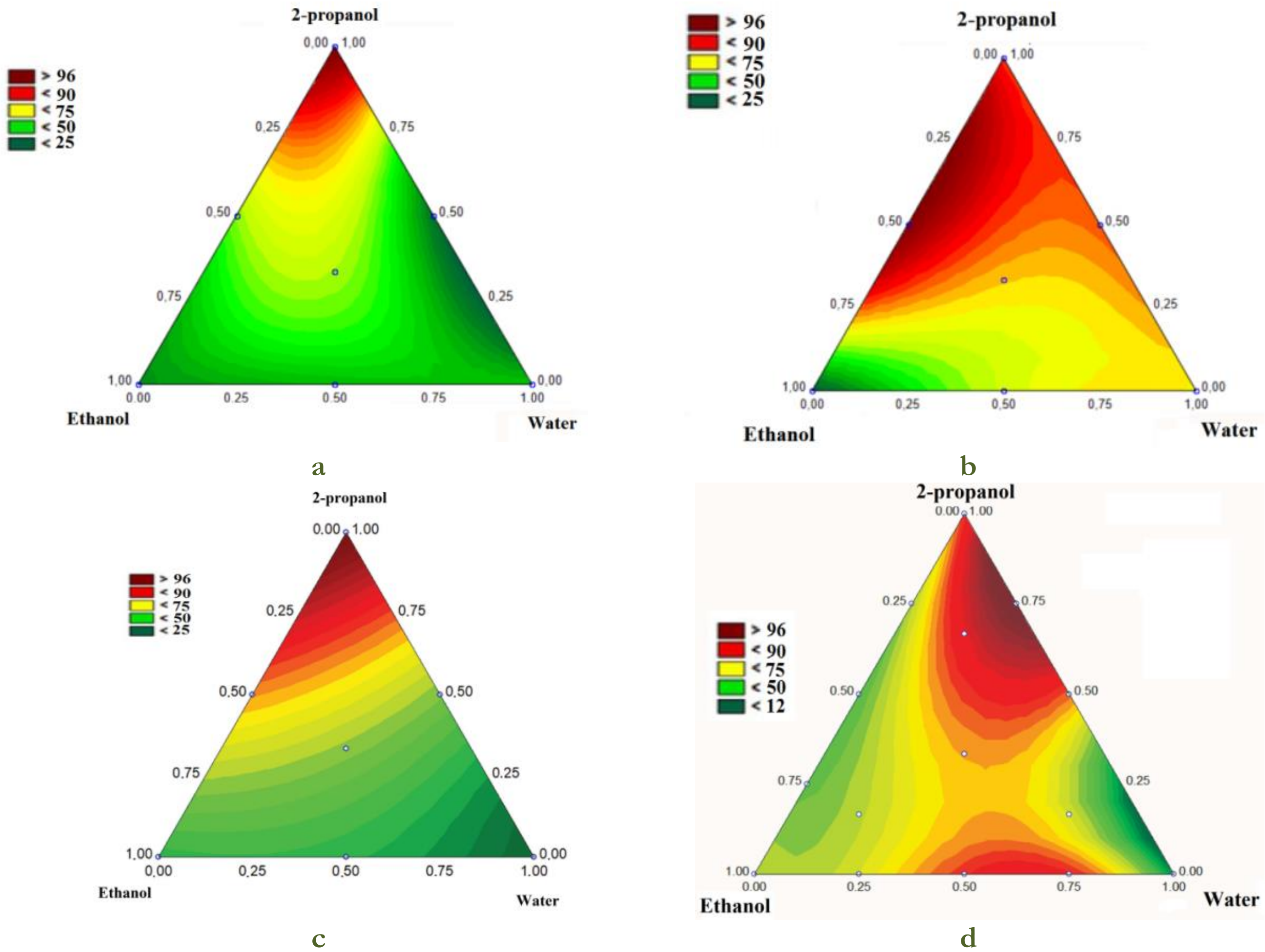

Fig. 3. Dependencies of the total content of terpene compounds according to the results of GC-MS for grape cake (a), apricot (b), peach (c) and tomato (d)

It is natural that for the extraction of volatile compounds, the optimum zone is located almost at the top of the triangle, which indicates the effective use of propanol in an almost predominant amount. Depending on the type of plant material, the optimum zone shifts either to the binary mixture of *i*-PrOH:EtOH or *i*-PrOH:H_2O. Simplex analysis shows that the optimal composition of this mixture for the studied extracts is as follows: EtOH - 5 – 15 %; *i*-PrOH - 60 – 80 %; H_2O - 5 – 70 %.

In this way, summarizing the results of optimizing the composition of the extractant mixture according to the criterion parameters of the content of polyphenolic compounds, flavonoids and the content of volatile compounds and taking into account the purpose of extractant selection, which would collectively contribute to the extraction of a wide list of the above-mentioned classes of compounds, the *i*-PrOH-EtOH-H_2O extractant system in the ratio in the range of *i*-PrOH - 50 – 40 %; EtOH - 25-30 %; H_2O - 15-25 % according to calculations based on experimental data is predicted to be the most optimal. Corresponding simplex lattice plans were built and implemented, where the inhibitory effect was chosen as the response function (Fig. 5).

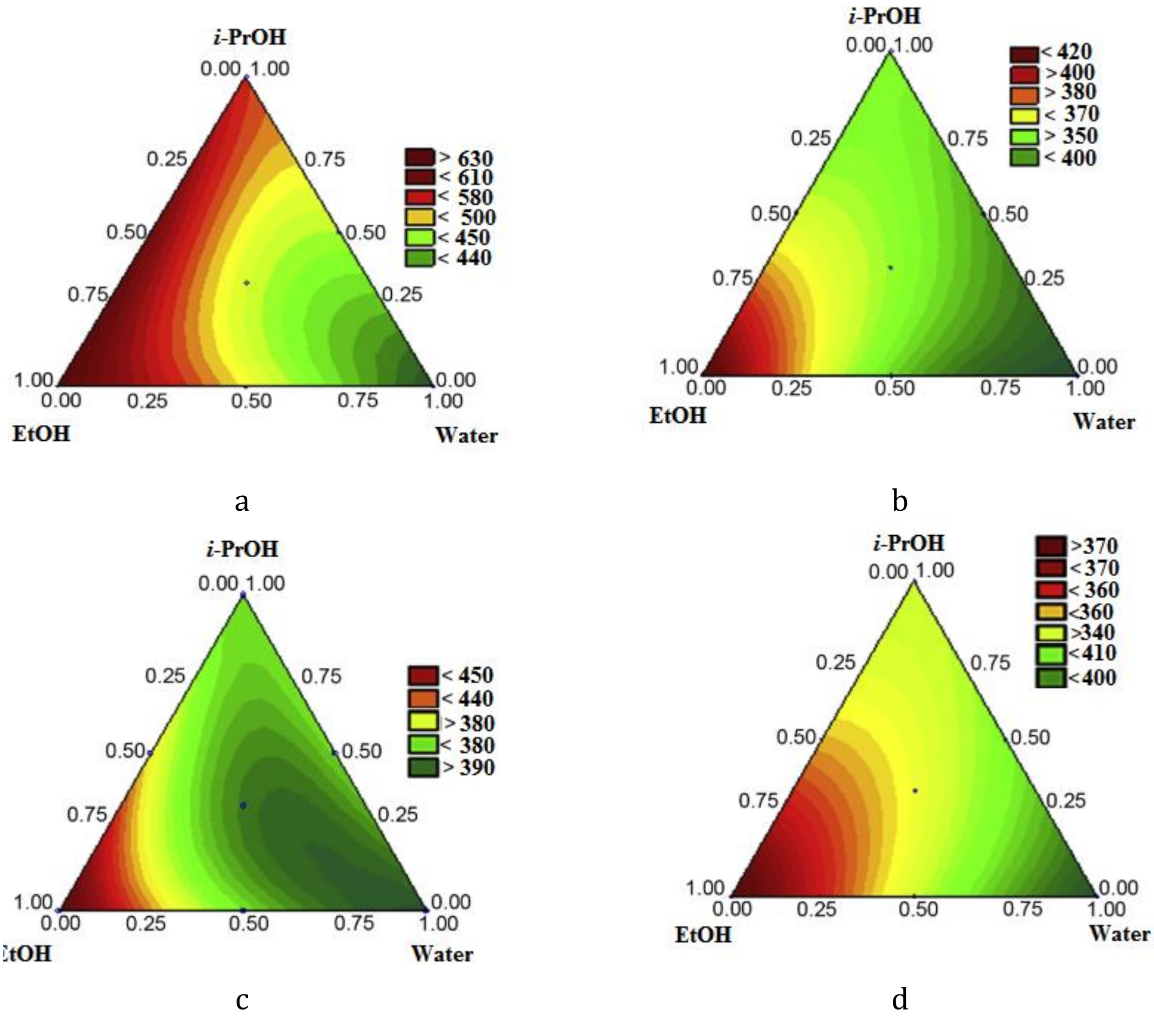

Fig. 4 Change in total antioxidant activity depending on the type of solvent for grape (a), apricot (b), peach (c) and tomato cake (d)

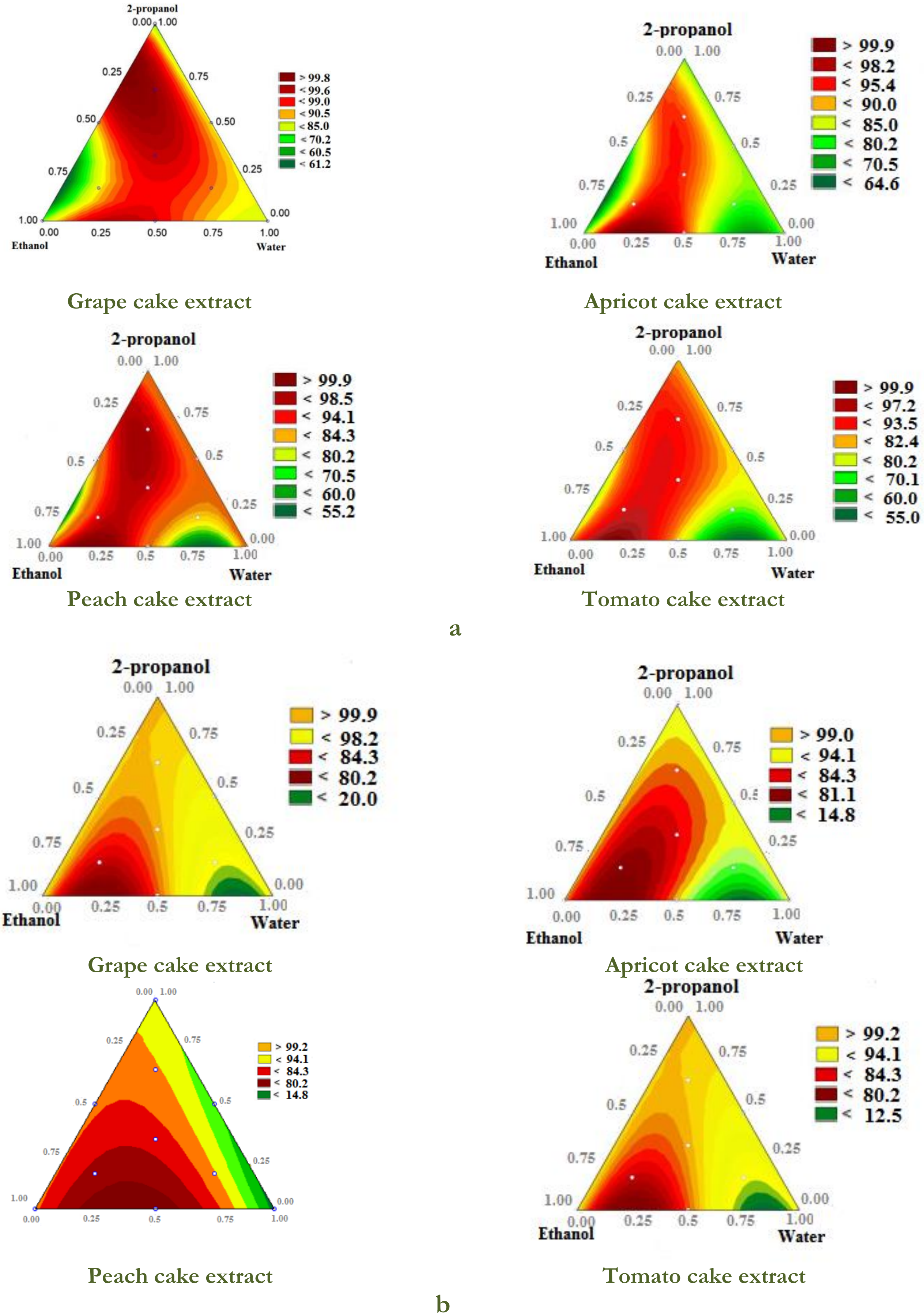

Fig. 5. Dependence of the degree of protection of steel in aqueous solutions (a) and in atmospheric corrosion conditions (b) on the composition of the i-PrOH-EtOH-H_2O solvent

The dependence of the degree of protection of steel in aqueous solutions (NaCl) and in conditions of atmospheric corrosion (conditions of periodic condensation of moisture) on the composition of the solvent used for the extraction of plant raw materials was established. The effectiveness of inhibition was determined by the gravimetric method within 20 days. It has been confirmed that sufficient inhibition efficiency is expected when using extracts obtained with an optimized solvent composition, *i*-PrOH-EtOH-H_2O extractant system in a ratio in the range of *i*-PrOH – 50 – 40 %; EtOH - 25-30 %; H_2O - 15-25 %.

Taking into account the established percentages of the components of the mixture of extractants, the calculated values of the polarity indices for the system vary from ~5.8 to 6.3. For further use, the system in the ratio of *i*-PrOH-EtOH-H_2O/45:30:25 (polarity index 6.37) was selected as optimal and further used as a solvent for the extraction of plant raw materials and to evaluate the inhibitory efficiency in various corrosive environments as a multifunctional corrosion inhibitor.

It was established that the optimal use of the *i*-PrOH-EtOH-H_2O extractant system with a percentage ratio of solvents in the range of 50-40 %; 25-30 %; 15-25 %, respectively. The calculated polarity index is in the range of ~ 5.87 - 6.37 and is a criterion parameter for the system of extractants relative to the studied raw materials. By comparing the areas of optima with the construction of simplex lattice plans where the inhibitory effect is selected as the response function (Fig. 5), it was established that the criterion parameters of the component composition of the extracts for their use as multifunctional inhibitors are the total content of phenolic compounds at the level of ≥ 90-150 mg of the extract, flavonoids ≥ 22-56 mg of extract and 70-96 mg of terpene compounds per 100 extract, total antioxidant activity in the range of ≥ 350-470 mg ascorbic acid equivalent/g extract (mg ASA/g extract). This approach regarding the use of *i*-PrOH-EtOH-H_2O/45:30:25 was used for the extraction of plant raw materials of other representatives of the processing products of fruit and berry crops [8]. A high inhibition efficiency of the obtained extracts was established in the two investigated corrosion conditions/environments (Tables 1-2).

Table 1

The degree of inhibitory efficiency of steel when using a solvent relative to other types of raw materials (21 days of anti-corrosion tests)

Extract	Inhibitory efficiency, IE %	
	As volatile corrosion inhibition Conditions of periodic moisture condensation, film formation time 72 hours	3 % NaCl C=1500 ppm, t= 20 °C
Plum cake	99.4	96.5
Nectarine cake	99.0	97.3
Apple cake	98.4	95.6

Table 2

Indicators of antioxidant activity and component composition of fruit and berry processing products

Extract	Antioxidant activity, mg AsA/g extract	Total content of phenolic compounds mg / flavonoids Total content of phenolic compounds, HA/ Quercetin/ /100 g of extract	Total content of terpene compounds
Plum cake	460	128/39	74
Nectarine cake	492	144/42	75
Apple cake	410	147/30	72

Conclusions

Based on the results of determining the influence of the type of extractant on the quantitative total content of polyphenolic compounds, flavonoids and anthocyanins and the quantitative content of volatile compounds determined by the GC-MS method, the optimization of the three-component composition of the extractant system was carried out using the method of simplex-gradient planning with the construction of concentration triangles, and it was established that the use of the system *i*-PrOH-EtOH-H_2O extractants with a ratio in the concentration ranges of *i*-PrOH – 50 – 40 %; EtOH – 25-30 %; H_2O - 15-25 % is the most effective, the calculated value of the polarity index varies between ~ 5.9 - 6.37.

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