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PRESERVATIVES USED IN FOOD –ANTIOXIDANT ACTIVITY AND SPECTRA IN UV-VIS, MID-INFRARED REGION

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Abstract: Preservatives are added to protect processed foods against microbial contamination. Antioxidants are additives that prevent oxidation and lengthen the shelf life of food. Preservatives and antioxidants have different technological functions in food. The aim of the present study was to determine and compare the antioxidant activity by analytical spectroscopic methods of widely used and available preservatives in both the food industry and household, such as ascorbic acid, acetylsalicylic acid, citric acid, potassium sorbate, and sodium benzoate.

Keywords: Preservatives, Antioxidant activity, Ascorbic acid, Acetylsalicylic acid, Citric acid, Potassium sorbate, Sodium benzoate.

INTRODUCTION

Every product of food production requires both basic raw materials and added ones. The food additives are used to maintain or enhance the food's freshness, safety, flavor, texture, or appearance. The additives also serve multiple purposes in food. In Europe, the word "additive" is preceded by the capital letter "E" and three numbers. Preservatives belong to food additives.

EXPOSITION

Preservation and type of preservation

Preservation is any process by which food can be protected from spoilage. The reason for the deterioration may be its oxidation, development of unwanted microorganisms such as bacteria, molds, and yeasts. Drying, smoking, salting, controlled fermentation (including pickling), sugaring, and the use of specific spices as antiseptics and preservatives are examples of traditional preservation techniques. Freezing, pasteurization, sterilization, irradiation, and the use of chemical preservatives are some contemporary methods of preservation. (<https://www.britannica.com>; Malchev, E., Mollov, P., 2008).

Every food has an expiration date; chemical preservatives help to extend the shelf life. Chemical compounds that hold back or prevent the growth of molds, yeasts, and bacteria in food products by preventing unwanted changes from occurring are called preservatives.

Antioxidants are additives to food products used to protect or delay their rancidity due to oxidation. In this way, the result is a longer shelf life. They are important to the food industry as they allow food products to keep their quality and nutritional properties. Antioxidants do not improve the quality of food, but they help preserve it for a longer shelf life. There is a great variety of natural and synthetic antioxidants used in food (tocopherols, ascorbic acid, rosemary extract, etc.).

Chemical preservatives and antioxidants

Chemical preservatives and antioxidants extend the shelf life of food by preserving the quality of the product, its organoleptic characteristics, and its nutritional properties. There are also differences between them which are explained by the intended use.

The most important difference between preservatives and antioxidants is their technological function. Both types of additives inhibit changes in the food product: preservatives

are inhibitors of biological changes (suppressing reproduction and preventing the spread of harmful microorganisms), while antioxidants are inhibitors of chemical changes (the oxidation of their components).

Another difference is their application in products of different nature: preservatives in water-containing food (in this environment, microorganisms such as fungi, bacteria, and yeasts that spoil food appear and develop), and antioxidants in food containing fats to protect against oxidation, the impact of light, heat, or other factors.

They also differ according to the classification used for nutritional supplements, which is used when they are written on the labels. The Codex Alimentarius refers to the International Numbering System (INS), which is used in Europe, with preservatives being E 200 to E 299 and antioxidants being the numbers between E 300 and E 399. (<https://www.btsa.com>)

The real chemical preservatives are most often acids: sulfuric, benzoic, sorbic, salicylic, etc. Their antimicrobial action is determined by the concentration of free and undissolved molecules and is favorably influenced by the higher active acidity of the environment. Substances that can have a preservative effect without being preservatives include ethyl alcohol, table salt, sugar, lactic acid, citric acid, ascorbic acid, etc. (Tanchev et al., 1983) They are also used as preservatives in the production of cans and foods for longer storage at home.

Chemical preservatives - types

Potassium sorbate (E 202) is used as a preservative in various foods (pickles, cheeses, mayonnaise, fruit juices, sausages, semi-finished meat products, and in some spices such as mustard) and cosmetic products. E 202 inhibits the growth of molds, yeasts and other microorganisms and thus increases the shelf life of food products.

Potassium sorbate is also used in wine after fermentation to stabilize it. It protects the wine from secondary fermentation by suppressing the development and proliferation of yeast cells. Potassium sorbate is an unsaturated fatty acid salt that is metabolized to CO₂ and water during fat metabolism.

Sorbate is harmless from a toxicological point of view. When combined with nitrites in the absence of sufficient ascorbate, the sodium salt of vitamin C, it is mutagenic (causes genetic mutations) (<https://foodadditives.net>).

Potassium sorbate and sodium benzoate are often used together because of their synergistic action in an acidic environment to protect against a greater variety of microorganisms.

Sodium benzoate (E 211) is the sodium salt of benzoic acid. It is a synthetic substance with preservative, healing and other functions. It is best known as a broad spectrum food preservative that is very effective against yeasts and bacteria but not so much against molds. It is used in foods and beverages with a pH of 4.0-4.5 or lower. Its effectiveness increases with decreasing pH. It is used in certain packaged foods, beverages, drugs, and cosmetics, as well as in personal care products and industrial products. Studies show that sodium benzoate can increase the risk of inflammation, oxidative stress, obesity, and allergies. E 211 can also turn into benzene, a potential carcinogen, but the low levels found in drinks are considered safe. Sodium benzoate is also used in pharmaceuticals because of its antimicrobial properties. It is included in the composition of tablets, capsules, and cough syrups (<https://foodadditives.net>). The medicine sodium benzoate is used to lower high levels of ammonia in the blood. It is also being studied for potential use in other conditions, including schizophrenia and multiple sclerosis (<https://www.healthline.com>).

Acetylsalicylic acid is not only a medicine; it is also an antiseptic in food preservation. When dissolved in hot water, aspirin is hydrolyzed. Hydrolysis products are acetic acid and salicylic acid. Salicylic acid, in low concentrations, inhibits the growth of yeasts and molds as well as some bacteria (Tanchev, S., Dimitrov, D. & Malchev, E. 1983). A solution of acetylsalicylic acid provides an acid reaction medium. That is why it is used for canning. Studies have shown that the use of aspirin as a preservative is inadmissible because it undergoes hydrolysis to produce salicylic acid, which in turn, at high temperatures (boils), is split into

phenol and carbon dioxide. Aspirin is used as a food preservative in households. Canned foods prepared using aspirin are not suitable for use.

Ascorbic acid (Vitamin C – E 300) is one of the most important nutrients needed by the body and is widely distributed in its natural form. It is mainly found in fruits and vegetables, especially tropical and citrus fruits; rose hips; cranberries; chilli peppers; black currants; fresh peppers; Brussels sprouts; lemon peel; parsley; dill; broccoli; cauliflower; red cabbage; strawberries, etc. Ascorbic acid also acts as a preservative to prevent spoilage of foods such as bread, cured meats, jams, and jellies. Due to the large number of beneficial effects on the human body, vitamin C is used as a food additive (E-number E300) and is included in a number of medicines against flu and cold diseases. (<https://framar.bg>; Zhong, Y., Shahidi, F., 2015).

Citric acid (E330) is a weak organic acid found in citrus fruits. It is one of the important metabolites in the Krebs cycle (citric acid cycle). It is used in preserving, freezing, and drying food. Citric acid acts as an acidity regulator, preservative, and food additive at the same time. It finds a place in the production of food products, chemical detergents and cleaning agents, medicine, and cosmetics. It prevents the spoilage of food caused by bacteria and the loss of its color (in freshly cut fruit, a solution of citric acid prevents browning in contact with air). An emulsifying agent is in the ice cream; it keeps the fats from breaking down. For modifying brewing water in home brewing. It finds applications in medicine, photography, the textile industry, etc. E 330 can be found in drinks, juices, sweets, and confectionery (<https://azchemistry.com>; <https://framar.bg>; Zhong, Y., Shahidi, F., 2015).

Determination of antioxidant activity of analyzed preservatives

The purpose of this study is to establish whether the preservatives used by the industry and households in food additives exhibit antioxidant properties and, if so, to what extent. The antioxidant activity of the preservatives was measured spectrophotometrically with a Cary 100 UV-VIS spectrophotometer using DPPH and FRAP tests. The results of both tests are expressed as $\mu\text{g/mol}$ Trolox equivalents (TE) per gram of active substance using standard curves (Zhong, Y., Shahidi, F., 2015).

The ferric-reducing power (FRAP) is a test that is based on electron transfer. This method measures the reduction of Fe^{3+} in the complex by the corresponding antioxidant in an acidic medium. Antioxidant activity was determined as an increase in absorbance, and results were expressed as $\mu\text{mol Fe}^{2+}$ Eq, or another similar antioxidant standard (Zhong, Y., Shahidi, F., 2015).

The radical scavenging method is an affordable and easy method for measuring antioxidant activity in foods. Antioxidants in complex biological systems, soils or liquid samples can be quantified by this method. One of the advantages of the method is that it reacts with all radicals in the sample (even antioxidants with lower activity) (Kedare, S., Singh, R., 2011; Zhong, Y., Shahidi, F., 2015).

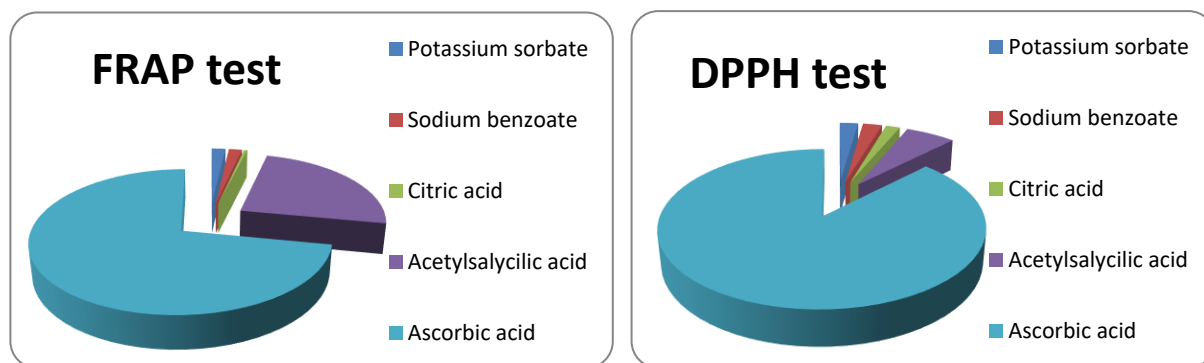


Fig 1. Pie charts of antioxidant activities determined FRAP test and DPPH test

The obtained data are presented as a pie chart because the difference between the most pronounced antioxidant activity from ascorbic acid and the least pronounced antioxidant with a preservative effect, citric acid, is very large. The two preservatives, sodium benzoate and potassium sorbate, have very similar antioxidant activities according to each of the tests used. According to the FRAP test, acetylsalicylic acid has higher antioxidant activity.

FT-IR and UV-VIS Spectrum

Fourier Transform Infrared Spectroscopy (FT-IR) preservative analysis was performed on powder samples. The measured spectra were recorded on a Bruker Tensor 37 FT-IR in the 4000-800 cm^{-1} region with an average of 128 scans in transmission mode with CaF_2 windows. The visible and UV spectra of the preservatives were taken on a Cary 100 UV-VIS spectrophotometer.

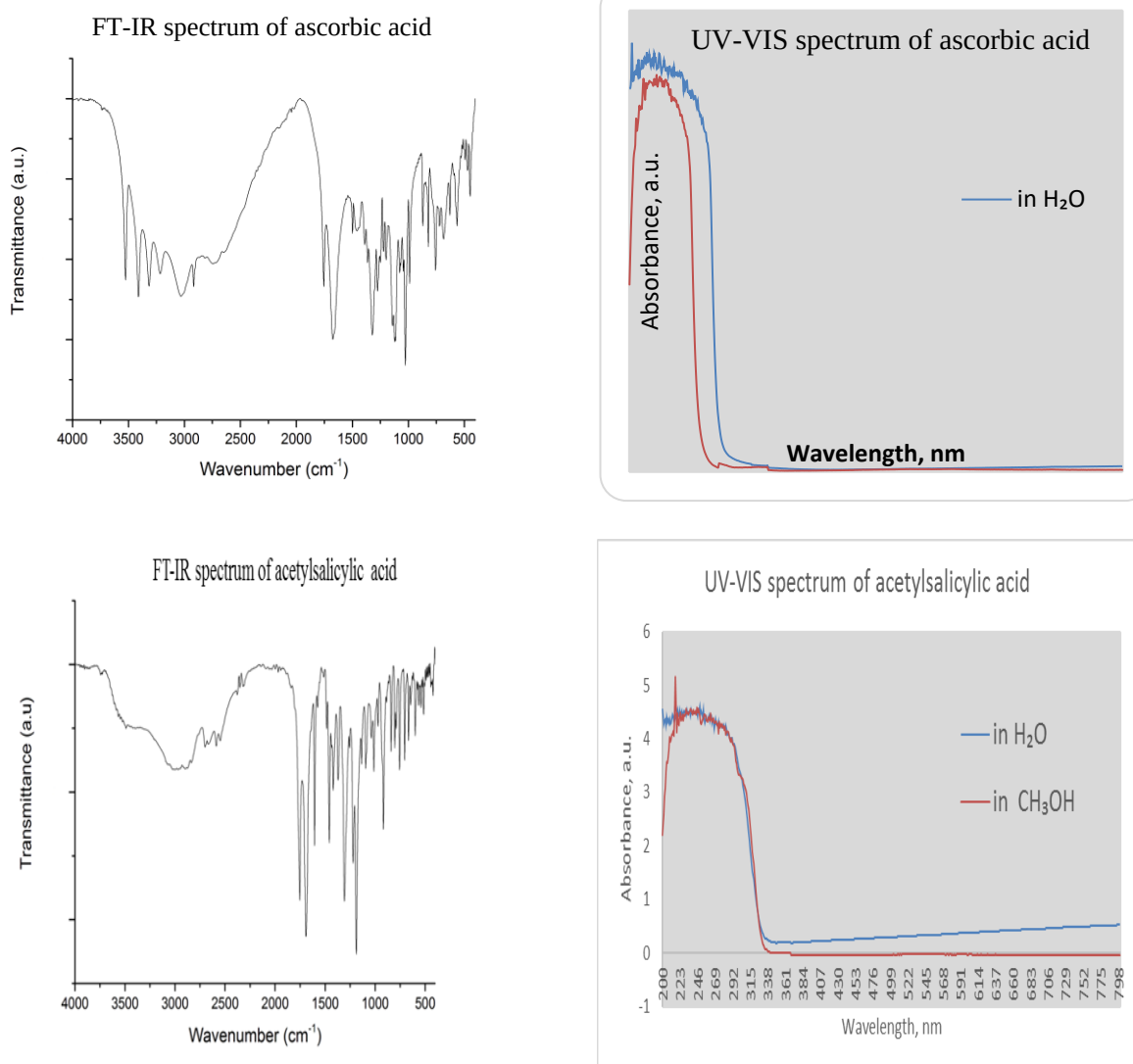


Fig 2. FT-IR and UV-VIS spectra of ascorbic acid and acetylsalicylic acid

The resulting spectra of studied preservatives only differ in the UV region; they do not have absorbance in the visible region. The acquired spectra in the FT-IR region are identical to the corresponding sample spectra in the databases.

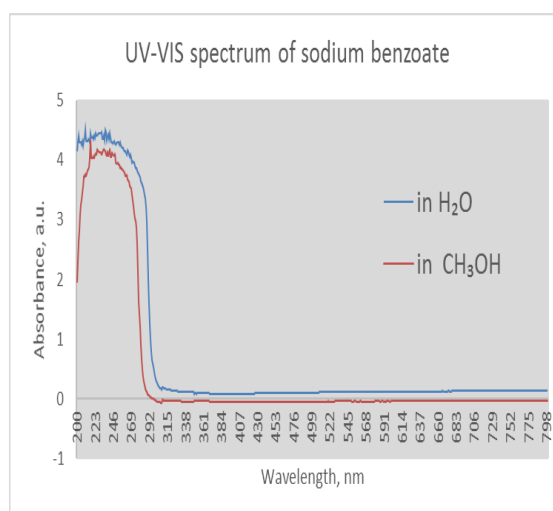
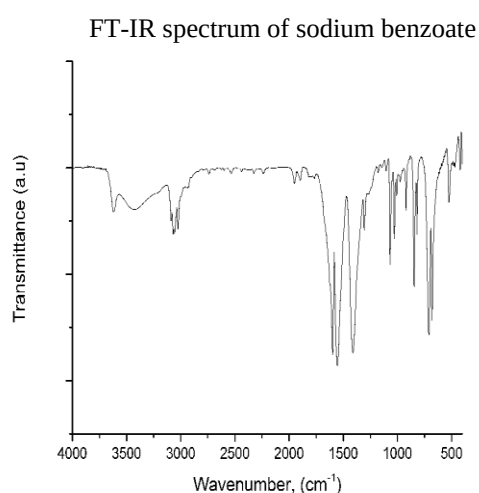
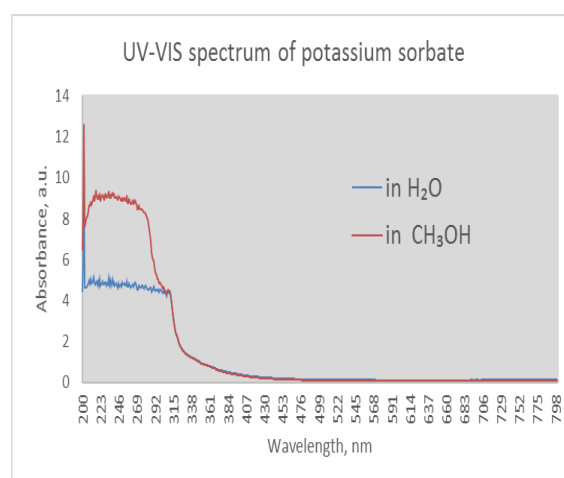
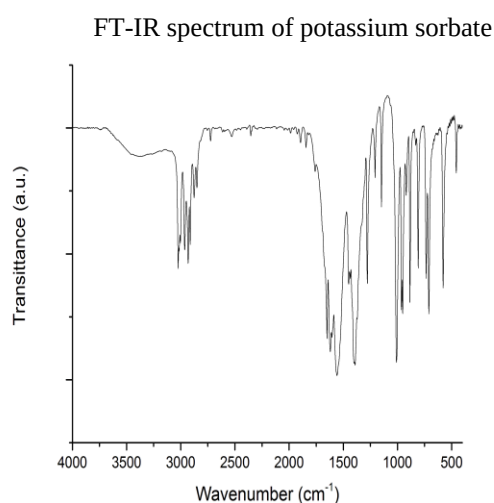
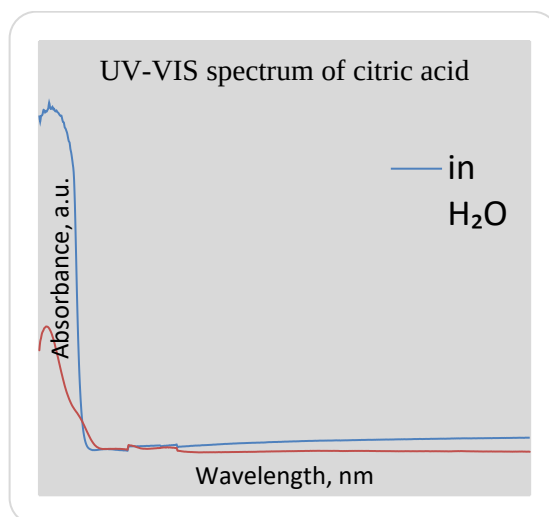
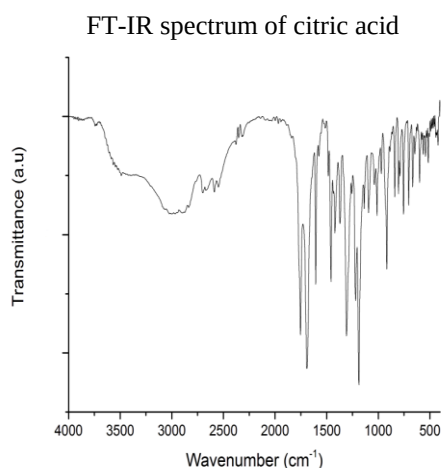


Fig. 3. FT-IR and UV-VIS spectra of citric acid, potassium sorbate, sodium benzoate

CONCLUSION

Citric acid has the lowest antioxidant activity, and ascorbic acid has the highest antioxidant activity measured by both DPPH and FRAP tests. These can be explained by the structure and

role they play in plant cells. Potassium sorbate and sodium benzoate have approximately the same antioxidant activity. The spectra taken in the mid-infrared region provide information about the functional groups of the studied preservatives.

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