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INVESTIGATING THE COMPARATIVE ANTIOXIDANT PARTITIONING IN FRIED OILS AND FRIED POTATOES: A SCIENTIFIC EVALUATION

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Abstract:

Frying is a complex process that enhances the attractiveness and flavor of the final product. In this specific investigation, potato slices were subjected to frying using sun flower oil, and an antioxidant was introduced at a concentration of 200 ppm in accordance with FDA guidelines. Both the potato slices and the frying oil were analyzed to determine the levels of antioxidants after several frying cycles. The primary objective of this research was to evaluate the distribution of butylated hydroxyanisole (BHA), tertiary butyl hydroquinone (TBHQ), and propyl gallate (PG) in the fried potato slices and the frying oils. To conduct the experiments, batches of 50 grams of sliced potatoes were fried at 180ºC for 3-5 minutes per batch. The results showed that TBHQ demonstrated a superior ability to retain antioxidants compared to the other two types. TBHQ experienced significant degradation at frying temperatures, which likely contributes to the stability of the frying oil. The by-products generated during this degradation process impede the radical chain elongation process. As a result, the effectiveness of the antioxidants followed this order: TBHQ > BHA > PG.

Keywords: Antioxidant, Fried oil, shelf life, carry through property

INTRODUCTION:

Fried sliced potato (French Fries) is a delicious traditional snack food. Among the various forms of sliced potato consumed fried Sliced potato are most acceptable due to its taste,

texture and palatability. Frying oil when heated it exposed to various chemicals and thermal reactions like hydrolysis, auto-oxidation, oxidative polymerization etc. During the frying process, it is possible to incorporate antioxidants into the cooking oil to prevent auto-oxidation and extend the shelf life of the oil used for frying. These antioxidants serve to delay the initiation or slow down the progression of oil oxidation by either inhibiting the formation of free radicals during the initial stage or by interrupting the chain elongation process, acting as either donors or acceptors of free radicals. In this particular study, we examined the effectiveness of three popular synthetic antioxidants, namely Butylated hydroxyanisole (BHA), tertiary butyl hydroquinone (TBHQ), and propyl gallate (PG), in their ability to carry through into the fried product as well as the frying oil. BHA is known for its high solubility in animal fats and its stability under the typical conditions encountered in various food-processing operations. TBHQ, another commonly employed synthetic antioxidant, exhibits excellent carry-through properties, effectively safeguarding fried food products from oxidative deterioration. Notably, it does not cause any discoloration and has no discernible impact on the taste or aroma of the final product. As for PG, it proves to be effective in preserving polyunsaturated fats. In all cases, the experiment utilized these three antioxidants at a concentration of 0.02% relative to the total oil or fat content of the food.

MATERIALA AND METHODS:

Materials

Potato (*Solanum tuberosum*) was purchased from a local market of Barrackpore city, cleaned and dried. Common salt was purchased from TATA brand. Sunflower oil was purchased from Meghdoot Oils Mill Pvt Ltd., Kolkata, India, was used as frying oil in the study. The antioxidants PG, BHA and TBHQ were purchased from Thomas Baker Ltd. The regents used were of analytical grade. 3-Methyl-2-benzothiazolinone hydrazone hydrochloride (MBHT) was procured from Sigma Chemicals.

Methods

Preparation of Sliced potato:

Sliced potatoes were prepared from washed, peeled potatoes. Peeled potatoes were blanched in salt solution (5% NaCl) for half an hour and then dried and cut into pieces vertically. 100 ml of sunflower oil was then used for frying for each batch contained 50 gm of sliced potatoes. The Sliced potato were dried in a tray drier at 40±1^{o}C to for 10 min and subsequently packed in polyethylene bags.

Extraction of fried oil remain in Sliced potato by Soxhlet method

Extraction of fried oil from sliced potato was done using Soxhlet extraction for 16 hr with petroleum ether (60–80 ^{o}C). The solvent was evaporated and the oil extracted was analyzed for the content of propyl gallate.

Estimation of propyl gallate

The estimation of Propyl Gallate (PG) was conducted following the procedure outlined in protocol 47.2.04, as per the AOAC (Association of Official Analytical Chemists) guidelines from 1984. The primary steps of this method are detailed as follows:

Preparation of Fat Solution: Initially, 40 grams of fat or oil were dissolved in a reagent consisting of petroleum ether and then diluted to a total volume of 250 mL with this same reagent. Gentle warming might be necessary to ensure complete solubility.

Separation: A 100 mL portion of the fat solution was transferred into a 250 mL separator. This solution was subjected to extraction with 20 mL of an aqueous solution containing 1.67% CH_3COONH_4, with continuous vortexing in a separating separator for a duration of 2.5 minutes. Once complete separation of the phases occurred, the aqueous layer was carefully drained into a 100 mL volumetric flask, taking care not to allow any oil droplets to enter the flask. This extraction process was repeated twice using 20 mL portions of the 1.67% CH_3COONH_4 solution, and the resulting aqueous layers were combined in the volumetric flask

Final Extraction: Subsequently, the fat solution underwent a final extraction with 15 mL of H2O for a period of 30 seconds. The aqueous layer from this step was combined with the previous washings, and at each stage, the layers were allowed to completely separate.

Dilution and Filtration: Exactly 2.5 mL of a 10% CH_3COONH_4 solution was added to the combined extracts in the volumetric flask, followed by dilution to volume with H2O. This solution now contained 1.25% CH_3COONH_4. It was then subjected to filtration through filter paper to eliminate any turbidity.

Final Measurement: An aliquot of the filtered extract, less than 20 mL in volume, was pipetted into a 50 mL glass-stoppered Erlenmeyer flask. It was then diluted to 20 mL with a 1.25% CH_3COONH_4solution. To this solution, 4 mL of H_2O and 1 mL of ferrous tartrate reagent were added. The contents were thoroughly mixed, and the absorbance was measured at 540 nm using a spectrophotometer, with a reference blank solution containing 20 mL of 1.25% CH_3COONH_4solution, 4 mL of H2O, and 1 mL of ferrous tartrate reagent.

Quantification: The quantity of PG present in the sample was determined using a standard curve.

Estimation of BHA and TBHQ

Oil from sliced potato was extracted using Soxhlet extraction for 16 h with petroleum ether (60–80 ^oC). The solvent was evaporated and the oil extracted was analyzed for the content of propyl gallate. BHA and TBHQ were estimated by the method given by (Prasad *et al.* 1987). The quantification of antioxidants in this study was carried out using a combination of 3-methyl-2-benzothiazolinone hydrazone hydrochloride (MBTH) and ceric ammonium sulfate. Specifically, TBHQ and BHA, both of which contain one or more phenolic hydroxyl groups, were subjected to a reaction with MBTH in the presence of cerium (IV) to produce colored

oxidative coupling products that resemble the reaction between MBTH and phenols (Gasparic et al., 1977). Under the specified reaction conditions, MBTH (I) undergoes oxidation, losing two electrons and one proton in the process, leading to the formation of an electrophilic intermediate (II) which serves as the active coupling species. This intermediate (II) then engages in electrophilic substitution reactions with BHA or TBHQ (at the para position, or ortho if the para position is blocked), resulting in the creation of the colored species (III). This color change can be used to quantify the presence of antioxidants like TBHQ and BHA in the samples under investigation.

Estimation of BHA and TBHQ

In the described procedure, a sample of oil or fat (10 grams) was initially dissolved in 50 mL of carbon tetrachloride. This solution was then subjected to extraction using four separate 20 mL portions of a 50% aqueous alcohol solution. The combined alcoholic extracts resulting from these extractions were subsequently concentrated by evaporation to reduce the volume to 5 mL. Afterward, the concentrated solution was diluted with water to achieve a final volume of 100 mL within a standard flask. The solution was then filtered through dry paper after being neutralized with 1 gram of calcium carbonate.

To quantify the antioxidants present in the samples, 3-methyl-2-benzothiazolinone hydrazone (MBTH) and cerium (IV) were added to the filtrate. For TBHQ analysis, 1 mL of cerium (IV) and 2 mL of MBTH were introduced, and the mixture was heated at a temperature ranging from 90 to 95°C for a duration of 15 minutes. The absorbance of the resulting solution was measured at a wavelength of 500 nm. In the case of BHA analysis, 0.5 mL of cerium (IV) and 3 mL of MBTH were added, followed by heating at a temperature between 90 and 95°C for 10 minutes. The absorbance of the solution was then measured at a wavelength of 480 nm. The concentrations of TBHQ and BHA in the samples were determined by comparing the measured absorbances to standard curves. In the study itself, sliced potatoes were fried in sunflower oil, and 200 ppm (parts per million) of antioxidants (PG, BHA, or TBHQ) were added to the frying oil in accordance with FDA specifications.French fries and oil were both analyzed for antioxidant content after repititive frying cycles (five cycles were detected). A batch of 50g Sliced potato were fried at frying temperature of 1800^{o}C and frying time for 3-5min for Sliced potatoes.

Results and Discussion

PG, TBHQ and BHA all were added at 200 ppm separately in sun flower oil. Standard curves of PG, TBHQ and BHA were prepared with concentrations ranging from 50,100,150,200 ppm (y=0.004x, coefficient of regression=0.995). Antioxidant partitioning behaviour of the referred three antioxidants was tabulated in **Table 1.** It was observed that propyl gallate was not detected in fried sliced potatoes at all. It indicates that propyl gallate has very poor carry through properties. The low levels of PG (Propyl Gallate) detected in the oil could likely be attributed to its susceptibility to thermal degradation at frying temperatures. At high temperatures encountered during frying, the primary mechanism leading to the loss of antioxidants is their chemical degradation. Dobarganes *et al.* (1986) similarly reported the

loss of PG at frying temperatures, highlighting its thermal instability and susceptibility to chemical degradation as contributing factors. On the other hand, BHA (Butylated hydroxyanisole) was found in small quantities in the fried potatoes, suggesting that its ability to carry through from the frying oil to the final product was better than that of PG. However, it appears that the carry-through properties of BHA were not sufficient to maintain higher levels of this antioxidant in the fried potatoes. Carry though properties of BHA in sliced potato would be due to its stability at mild alkaline conditions (Emerton and Choi 2008) suggested the suitability of BHA in baked and fried foods. After first frying only 18.49 ppm was retained in the oil. The reason for this may be due to steam volatilization of BHA and thermal degradation. In BHA, the tertiary butyl group interferes with the antioxidant activity of the phenolic

Serial No.	Antioxidant Content (ppm)					
	PG		BHA		TBHQ	
	Oil	Potato sliced	Oil	Potato sliced	Oil	Potato sliced
Before frying	186	NA	174	NA	182	NA
Frying cycle						
1.	7.66±0.38	ND	18.49±0.33	8.24±0.43	38.49±0.33	14.24±0.43
2.	3.50±0.18	ND	11.76±0.18	6.67±0.22	20.76±0.18	9.69±022
3.	ND	ND	9.84±0.64	3.88±0.17	11.84±0.64	6.49±0.83
4.	-	-	3.29±0.33	ND	5.69±0.72.6	6±0.14
5.	-	-	ND	ND	ND	ND

All values are mean±SD, n=3 ; ND=Not detectd;

Propyl Gallate (PG), Butylated Hydroxyanisole (BHA), Tertiary Butyl hydroquinone (TBHQ)

Table 1: Antioxidant content (PG, BHA, TBHQ) in fried oils and fried sliced potatoes

group and structural steric hindrance is responsible for the low thermal stability (Dziezak 1986). TBHQ (Tertiary Butylhydroquinone) exhibited superior carry-through properties compared to both PG (Propyl Gallate) and BHA (Butylated hydroxyanisole) and was found in the fried sliced potatoes. TBHQ's effectiveness as an antioxidant extends even to high temperatures, as it acts as an inhibitor of chain radical processes. This observation aligns with previously published data across various lipid substrates (Dougherty 1993; Gordon and Kourimska 1995; Sanhueza et al. 2000), confirming its efficacy under different conditions.

Throughout the frying process, it was noted that the concentration of TBHQ decreased from 38.59 ppm to 5.69 ppm in the frying oil after four frying cycles. In the fried potatoes, a similar reduction was observed, with TBHQ levels decreasing from 14.24 ppm to 2.66 ppm. This decline in TBHQ concentration may be attributed to the generation of volatile compounds as a result of the antioxidant's thermal degradation. These volatile compounds could play a significant role in influencing the stability of oils during thermal processing. TBHQ (Tertiary Butylhydroquinone) has been observed to undergo significant degradation at frying temperatures, leading to the formation of numerous decomposition products.

Conclusions:

Antioxidants are added to oil in order to enhance the shelf life of oil and of the fried product. Propyl gallate, BHA and TBHQ are major antioxidants that had been used in present study to prevent lipid oxidation. Propyl gallate showed poor carry through properties and was not detected in fried sliced potato. Also it was present in very less quantity in frying oil indicating it to be ineffective at frying temperatures. BHA showed better carry through effect compared to propyl gallate and was detected in fried sliced potato and oil. TBHQ showed carry through property in fried sliced potato that was better than both propyl gallate and BHA. It is also effective antioxidant at frying temperatures. Thus it can be concluded that for frying sliced potato, the effectiveness of antioxidants is of the order TBHQ>BHA>PG.

FUTURE SCOPE:

Synthetic antioxidants find widespread application in the food industry where they serve to inhibit the oxidation of fats and oils within various food products. This crucial role in preventing oxidation contributes significantly to prolonging the shelf life of foods, thereby averting issues related to rancidity that can compromise the taste, texture, and nutritional quality of these products. In addition to food products, synthetic antioxidants are used in various industries, including cosmetics and pharmaceuticals, to maintain the quality and stability of the products. They prevent color changes, off-odors, and texture alterations caused by oxidation. It's crucial to use synthetic antioxidant within established safety guidelines and regulations to ensure that they do not pose any health risks. Additionally, there is a growing trend toward using natural antioxidants due to consumer preferences for clean-label products.

Conflict of Interest: The authors of this paper declare that there are no conflicts of interest associated with the publication of this research paper.

Author's Contribution: Tanushree Mondal undertook the entire literature review. Sayantani Chitra was responsible for creating all the figures and handling the references. Dr. Rupali Dhara Mitra conceptualized the idea and title of this paper and also provided comprehensive editing for the entire manuscript.

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