

Effects of non-thermal plasma sterilization on volatile components of tomato juice

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Abstract Pasteurization is an important issue to keep from fruit decay due to microbes for fruit preservation. Conventional heat sterilization is based on thermal process. However, the flavor and nutrition components can be changed by heat damage. In this study, an apparatus was designed to produce non-thermal plasma (NTP), which can be applied in fruit sterilization. NTP can be generated through electric discharge in gaseous chamber. A simple NTP reactor may consist of two electrodes with a chamber and connected to a high-voltage power supply. The new technique of NTP was applied to keep fruit fresh. After the tomatoes were treated by NTP, the volatile flavor components were analyzed by GC–MS and were compared to heat treatment and non-treatment. The results showed that the quality of fresh tomato fruit was unaffected by plasma disinfection treatment, and the contents of trans-2-hexenal and n-hexanal were significantly higher than that by heat processes. NTP has less effect on volatile chemical compositions of tomato juice. NTP technology is a promising method for food pasteurization in the future.

Keywords Non-thermal plasma · Tomato juice · Sterilization · Volatile component

Introduction

Different fruit and vegetable juices have their own unique smells and the main flavor components including esters, alcohols, aldehydes, acids also as an important evaluation indicator of product quality, and most of them are volatile components (Hayase et al. 1984; Salles et al. 2003; Riu-Aumatella et al. 2004). During the heat processes, it is difficult to avoid destruction of volatile substances, causing the deterioration of flavor (Servili et al. 2000). In recent years, many scholars have studied the non-thermal sterilization technology; Ma Hongbing and others used plasma technology for liquid food sterilization, and they found that this technology enables the total number of bacteria in fresh juice and milk decrease five logarithms (Ma et al. 2002; Lin et al. 2006). Non-thermal plasma (NTP) generated by corona discharge could inactivate *E. coli* in apple juices; after plasma treatment for 40 s, the number of *E. coli* decreased five logarithms (Deng et al. 2007). After non-thermal plasma for decontamination of *E. coli* in milk, the initial pre-plasma bacterial count of 7.78 Log CFU/mL in whole milk was decreased to 3.63 Log CFU/mL after 20 min of plasma application. Non-thermal plasma did not cause any significant change to the pH and color values of raw milk samples. The novel NTP system tested was able to significantly reduce *E. coli* in milk by more than a threefold log reduction without significantly affecting pH or color properties (Gurol et al. 2012). Some other scholars have also proved that non-thermal plasma had a significant effect in killing food microbes, such as bacterial, *Saccharomyces cerevisiae*, spore (Perni et al. 2008; Ermolaeva et al. 2012; Bayliss et al. 2013; Liu et al. 2013; Ma et al. 2013; Baier et al. 2013). An original non-thermal process to inactivate dehydrated

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bacterial spores has been applied (De la Noue et al. 2012). Compared with thermal processes, non-thermal plasma sterilization has significant advantages, such as at a lower temperature, short time. Meanwhile, low processing temperature retained the food nutritional content, color, flavor, and texture and maintained the freshness of products. With the loss of aroma reduced, as a result, some of the potential flavor components of juices are to be released. At same time, plasma effects on enzyme activity shows that cold plasma is capable of reducing the activity of both polyphenoloxidase (PPO) and peroxidase (POD) in the model food system. The activity of PPO was reduced by about 90 % after a treatment time of 180 s. POD was more stable and was reduced by about 85 % after 240 s (Surowsky et al. 2013). The research has indicated that n-hexanal was a characteristic flavor of tomato juices (Sebastiano et al. 1995). In this paper, the volatile components of tomato juice were extracted using the simultaneous distillation apparatus from untreated and non-thermal plasma-treated tomato samples at Food Processing Laboratory in Beijing University of Agriculture in the summer of 2011. The volatile components were analyzed with the GC–MS and compared with heat-treated tomato juice. Then the changes of hexanal components in tomato juice were studied, to provide evidences for future application of the non-thermal plasma sterilization technology in tomato-processing industry.

Materials and methods

Materials

Fresh tomato: “San-Bao” variety were purchased from Beijing Xiaotangshan agronomic Park and stored below 4 °C. Saturated calcium chloride, sodium hydroxide, anhydrous ether, analytical grade, were purchased from Beijing Chemical Reagent Company; Preparation of tomato juice

Raw materials → peeling → cutting → juicing
→ non - thermal plasma treatment

Freshly squeezed tomato juice were filled in sterile polyethylene bottle, sealed immediately, and preserved it in a refrigerator at 4 °C for reserve.

Tomato juice sterilization process

Tomato juice was sterilized by heat sterilization (85 °C for 30 min) or by equipment shown in Fig. 1, which could produce electric plasma at high-voltage power supply (10 kV at 30 °C for 5 min).

Non-thermal plasma equipment was supplied by Nanjing Suman Electronics Corporation; Agilent 6890 N GC–MS, USA, with G1701MSD ChemStation and NIST02 standard library; Simultaneous distillation device was purchased from Beijing Glass Instrument Factory. Self-made liquid plasma sterilization tube, as shown in Fig. 1. Tomato juice was pumped into apparatus through inlet 7 by a peristaltic pump. When it passed through bubbling device 6, it was mixed with the air to form homogeneous bubbles. Currents were produced by NTP supply and passed to inner electrode 3. Electric discharge was produced between inner electrode 3 and ground electrode tube 5; meanwhile, reactive free radicals were produced. The microbes in tomato juice were inactivated by reactive free radicals in the chamber. Then sterilized juice overflowed from outlet. The components of treated juice were analyzed.

Simultaneous distillation–extraction

Take 200 mL of tomato juice sample in a 250-mL round-bottomed flask and weighed 40 mL of the distilled diethyl ether in a 100-mL round-bottomed flask; simultaneous distillation–extraction for 2 h is carried out, and stop heating until it cools down. Add a small amount of anhydrous sodium sulfate (about 2–3 g) in a 100-mL flask and dry it for 2 h to remove water. After pouring into 80-mL concentrate bottle, the dried sample then was incubated in water bath at 40 °C. It was carefully concentrated to

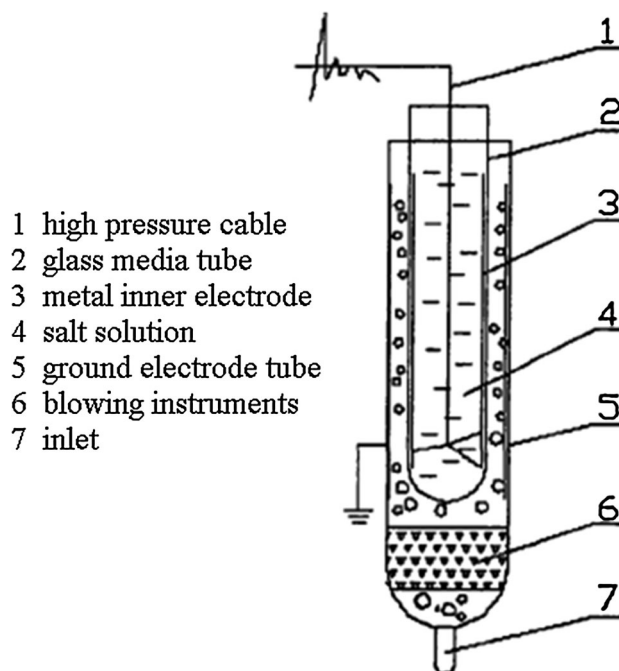


Fig. 1 Schematic of experimental layout



Table 1 Flavor compounds identified in non-thermal plasma-treated, original, and heat-treated tomato juice by GC–MS analyze

Number	Retention time (min)	Components	Compositions (%)		
			Neat juice	Non-thermal plasma-treated	Heat-sterilizing treated
1	3.383	2-Ethoxy-pentane	1.16	0.78	0.15
2	4.024	Cycloheptatriene	0.24	0.22	0.20
3	5.133	Hexanal	0.16	0.26	–
4	5.647	2-Ethoxy propane	0.26	0.32	0.07
5	6.139	1-Ethoxy-2-propanol	32.64	55.83	83.6
6	7.477	Trans-2-hexenal	–	0.09	–
7	7.649	Ethylbenzene	0.25	0.20	0.25
8	8.137	Inter-xylene	–	0.07	0.10
9	8.241	O-Xylene	–	0.04	0.05
10	9.380	Styrene	0.39	0.38	0.68
11	10.977	L-threitol	–	0.58	0.68
12	12.994	Acetal	1.29	1.86	1.06
13	16.147	Ethyl laurate	1.98	–	–
14	16.333	3-Nitropropionic acid	2.04	–	–
15	18.239	2-Methyl-1,3-dioxolane	3.41	15.03	0.59
16	19.044	Acetal	10.38	2.5	–
17	19.837	2-Methyl-1,3-dioxolane	–	0.31	–
18	22.859	Octyl formate	39.5	–	–
19	24.239	2-Methyl-1,3-dioxolane	–	0.8	–
20	26.914	Glycerol	–	4.96	3.67
Total			94	85	94



Fig. 2 Total ion current chromatogram of GC–MS of tomato juice

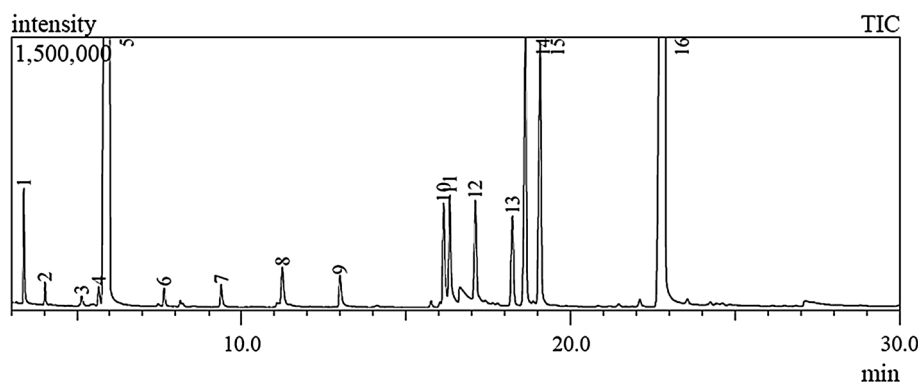


Fig. 3 Total ion current chromatogram of GC–MS of non-thermal plasma-treated tomato juice

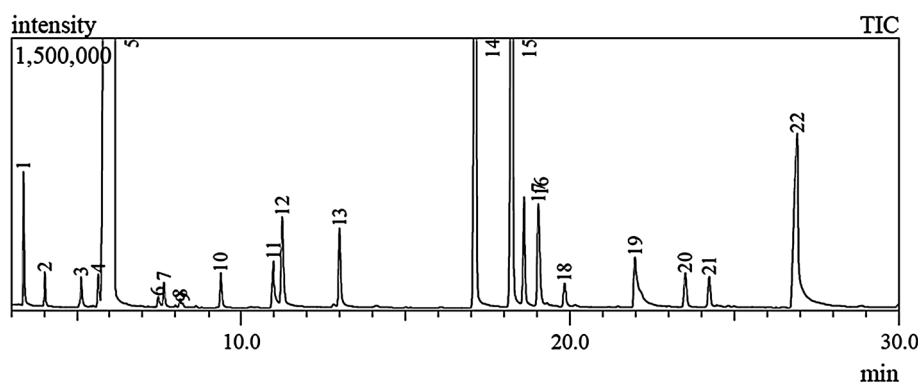
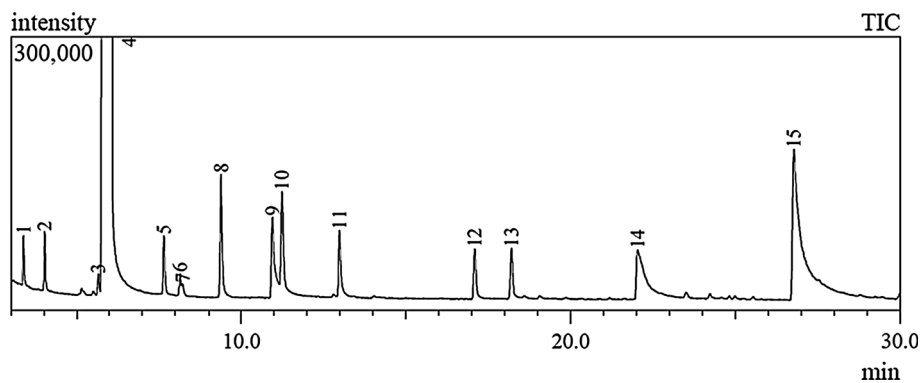


Fig. 4 Total ion current chromatogram of GC–MS of heat treatment tomato juice



2.0 mL by Vigreux column, and then 1 μ L was taken for GC–MS analysis (Tian et al. 2009).

GC–MS analysis

Chromatographic conditions: HP-5 capillary column (30 m \times 0.25 mm \times 0.25 μ m), 50 $^{\circ}$ C as the starting temperature and maintained for 2 min, heated to 110 $^{\circ}$ C with the rate of 8 $^{\circ}$ C/min, and then raised to 220 $^{\circ}$ C (6 $^{\circ}$ C/min), and finally raised to 240 $^{\circ}$ C (10 $^{\circ}$ C/min), maintained for 1 min; inlet temperature is 250 $^{\circ}$ C; injection volume 1 μ L; split ratio 5:1, solvent delay of 3 min. MS

conditions: ion source temperature of 250 $^{\circ}$ C; transfer line temperature of 250 $^{\circ}$ C; EI as the ionization mode, emission current 200 μ A; electron energy of 70 eV; scanning the mass range of 50–650 amu.

Results and discussion

After the GC–MS separation and identification, 16 kinds of ingredients were isolated from un-treated tomato juice, accounting for 94 % of the total mass fraction; 20 kinds of ingredients of tomato juice were isolated from non-thermal



plasma sterilization treatment, accounting for 85 % of the total mass fraction. Fifteen kinds of components were isolated from thermal sterilization, representing 94 % of the total mass fraction, as shown in Table 1. These volatile components mainly composed of hydrocarbons, esters, alcohols, aldehydes, acids, and other substances. From Table 1, it can be seen that after the non-thermal plasma treatment, trans-2-hexenal, m-xylene, o-xylene, L-threitol, and glycerol of tomato juice are increased, and lauryl ethyl 3-NPA reduced. From chromatogram, the content of key mediate of hexanal (with the retention time of 5.133 min) in neat juice was 1.6 times less than that in nonthermal plasma treated juice (Figs. 2, 3). However, hexanal components were totally disappeared after heat treatment (Fig. 4). This showed that non-thermal plasma treatment has a certain effect on the volatile components of tomato juice. A larger proportion of volatile components of tomato juice, 1-ethoxy-2-propanol, increased 71.8 % after non-thermal plasma treatment, while increased 256.4 % with heat sterilization, indicating that after heat sterilization treatment, the evaporation composition of tomato juice changed significantly higher than non-thermal plasma treatment. Meanwhile, non-thermal plasma treatment has less effect on volatile chemical components of tomato juice. Compared with ultra-high-pressure processing (HHP) (Butz et al. 2003; Boulekou et al. 2011; Augusto et al. 2013), non-thermal plasmas are emerging and promising technologies for sanitation because they are both efficient and cheap (Moreau et al. 2008).

Volatile components in tomato juice were determined by GC–MS. The effects of different treatments were analyzed. The main results indicated as follows: five new substances were produced by non-thermal plasma-treated tomato juice, such as anti-2-hexene aldehyde, and two substances were lost, such as ethyl laurate. The hexanal content of non-thermal plasma-treated tomato juice had increased by 1.6 times. Non-thermal plasma treatment had no significant effect on the smell of tomato juice, but the change of heat sterilization was significantly higher than that of non-thermal plasma treatment.

Conclusion

The effect of non-thermal plasma sterilization technology for fruit and vegetable juice beverage flavor was first studied. The NTP treatments were simple and quick and have less impact on flavor and aroma of tested samples by the analysis data. Bacteria can be killed and residues can be cleared away through the gas circulation system. The produced plasma is limited within a containment system, causing no harm to the operator. The advantages of NTP technology are time saving, low operating temperature, and

keeping fruit fresh. The technology can be widely used in a variety of fruits for sterilization. Non-thermal plasma sterilization technology can keep the original flavor and nutrients of food and is expected to replace existing thermal pasteurization food processes.

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