Changes in chemical characteristics of market paneer samples preserved with formalin

Richa Singh, Darshan Lal, Vivek Sharma and Priyanka Singh Rao

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Abstract
Paneer is an acid cum heat coagulated milk product and is widely consumed in the northern part of India. When food safety officers collect the paneer sample for analysis, formalin is added to keep it fit for longer duration for chemical analysis. In India, 0.4% formalin is a legally permitted preservative. However, scientific reports suggest that it is not able to preserve paneer samples for long duration. At 0.4% concentration all microorganisms are not killed and consequently the spoilage of paneer is not prevented. Therefore, in the present study various physicochemical properties of 0.4% formalin-preserved paneer (formalin added by spraying method) were determined during its storage at room temperature. It was found that % acidity, water soluble nitrogen, tyrosine value, OPA content, FFA, peroxide value, conjugated diene and total carbonyl content of paneer increased significantly after one month of storage at 37°C. Based on the results obtained, it may be concluded that in the paneer samples which are preserved with 0.4% formalin (added by spraying method), changes in chemical characteristics of paneer were observed just after 1st month of storage and after 2nd month of storage there was excess gas production and very foul smell due to growth of microorganisms.

Keywords: Formalin, paneer, physico-chemical properties, FSSAI

Introduction
Paneer represents a South Asian variety of soft cheese obtained by acid and heat coagulation of milk. It is non-fermentative, non-rennet and un-ripened type of cheese (Chandan, 2007). Food safety officers, appointed by FSSAI (Food Safety and Standard Authority of India) collect the food samples from market for analysis (checking its quality), and adds a preservative (except in the case where the sample is meant for microbiological analysis) for the purpose of maintaining the collected samples in a condition fit for analysis. Formalin (40% aqueous solution of formaldehyde) is the only legally permitted preservative for milk and milk products meant for analytical purpose, in the proportion of 0.1 ml (two drops) for 25 ml or 25 grams, amounting to 0.4 ml (Eight drops) for 100 ml or 100 grams. Considerable time is involved in the legal procedures starting from the time of collection of the sample to the stage of its analysis at the first instance at the Food Analyst level and to the stage of its analysis at the secondary level in the referral lab (Central Food Laboratory) in case of litigation. In the present investigation, the paneer samples were prepared by cutting cubes (0.8-1 cubic cm) with knife and the mode of addition of formalin (0.4%) is done by spraying method (5 mL sprayer). The changes taking place in physico-chemical properties during storage of paneer with 0.4% formalin were observed.

Materials and Methods
Collection and preparation of paneer samples
The samples of paneer manufactured and sold by local dairy and shops of Karnal market were collected. Paneer samples (250 g) were cut in cubes (0.8-1 cubic cm) and stored in screw capped wide mouth autoclaved bottles (500 mL capacity). 0.4% formalin (permitted by FSSAI) was added by spraying method (5 mL capacity sprayer), after closing the bottle with caps, mixing was done thoroughly by inverting the bottles 8-10 times. Samples were stored at 37°C for 6 months and analyzed at every one month intervals for physico-chemical parameters. Paneer samples without formalin (control) were

Richa Singh (✉), Darshan Lal, Vivek Sharma and Priyanka Singh Rao
Dairy Chemistry Division, ICAR-National Dairy Research Institute, Karnal 132 001, Haryana, India

Richa Singh
Dairy Chemistry Division
ICAR-National Dairy Research Institute Karnal - 132001
Ph. No. 0184-2259127, +91-9466963930
E mail: richasingh.ndri@gmail.com
also stored under identical conditions for one week and analyzed after every one day interval.

Analysis

The samples were analyzed for Acidity % lactic acid [IS: SP (Part XI), 1981], Water Soluble Nitrogen (Kosikowski, 1977), tyrosine value (Lowry et al., 1951) and O-phthaldialdehyde (OPA) content (Nielsen et al 2001), Free Fatty Acid % (Konicek, 1979), Peroxide value (IS, 1966), conjugated diene (AOAC, 1995) and total carbonyl content (Rama Murthy and Jain, 1973).

Results and Discussion

Data for titratable acidity for control and 0.4% formalin preserved paneer is presented in figure 1. The average acidity of fresh paneer was 0.69±0.02% lactic acid. On, addition of 0.4% formalin, the titratable acidity of paneer samples increased to 0.74±0.06% lactic acid. In control samples, acidity increased significantly after 1st day, continued to increase up to 4th day. On 5th day there was a small drop in acidity, thereafter it increased up to 7th day. With 0.4% formalin, acidity increased significantly after 1st month of storage and continued to increase till 3rd month. On 4th month there was a small drop in acidity and thereafter it increased up to 6th month.

Water soluble nitrogen (WSN), Tyrosine value and OPA content were taken as an indicator of proteolysis. Data for Water soluble nitrogen (WSN) content, Tyrosine value and OPA content for control and 0.4% formalin preserved paneer was presented in figure 2 and 3. The average WSN content, tyrosine value and OPA value of fresh paneer were 0.09±0.01%, 8.83±0.19 mg/100g paneer and 5.13±0.09 μg/g paneer respectively. On, addition of 0.4% formalin, these values were found to remain same as of fresh paneer. In control samples, WSN and tyrosine content increased significantly after 1st day and continued to increase up to 7th day. OPA value has increased significantly after 2nd day of storage. With 0.4% formalin, these values increased significantly after 1st month and continued to increase till 6th month.

Free Fatty Acid (FFA) is an indicator of hydrolytic rancidity. Data for FFA content for control and 0.4% formalin preserved paneer is presented in figure 4. The average FFA content of fresh paneer was 0.21±0.01% oleic acid. On, addition of 0.4% formalin, it was found to remain same as of fresh paneer. In control samples, FFA content increased significantly after 1st day and continued to increase up to 7th day. With 0.4% formalin, FFA content increased significantly after 1st month and continued to increase till 6th month.

Peroxide value, conjugated diene and total carbonyl content are indicator of oxidative rancidity. Data of control and 0.4% formalin preserved paneer for Peroxide value and conjugated diene is presented in figure 5 and for total carbonyl content is presented in figure 6. The average peroxide value, conjugated diene and total carbonyl content of fresh paneer were 0.08±0.01 milliequivalent peroxide per 1000 g of paneer, 0.70±0.02% and 6.04±0.09 μ moles/g of fat respectively. On, addition of 0.4% formalin, peroxide value and conjugated diene were found to remain same as of fresh paneer, however slight increase was observed in total carbonyl content. In control samples, these values increased significantly after 1st day and continued to increase up to 7th day. With 0.4% formalin, these values increased significantly after 1st month and continued to increase till 6th month.

Sachdeva and Singh (1990) reported that acidity of paneer vary from 0.20 to 1.17 %. Therefore, acidity of paneer in the present study was within the reported range. Increase in initial acidity on addition of formalin is well understood on the basis of well -known reaction of formalin with primary amino groups, amide groups and guanidyl groups of milk proteins liberating hydrogen ions, which are titrated against a standard alkali solution (Jenness and Patton, 1969; Bansal and Singhal, 1991, Boghra and Borkhatriya, 2003, Upadhyay et al, 2014). An increase in the titratable acidity of control sample was an indication of bacterial spoilage by lactose fermenting organisms. Decrease in acidity might be due to utilization of lactic acid and liberation of non-acidic products of protein decomposition. Similar increase and decrease in acidity was reported by Kumar and Bector (1991). In his study he reported initial titratable acidity of paneer 0.54 %, it increased slowly during storage and reached 0.9 % on day four and thereafter declined and reached a value of 0.59 % on day ten. According to Haridas and Narayanan (1976) titratable acidity of fresh paneer was 0.55%; however, titratable acidity for control and 0.4% formalin preserved paneer was 1.73% and 0.66% respectively after 21 days at room temperature.

Sachdeva and Singh (1990) reported 0.10% of soluble nitrogen content in paneer sample dipped in brine and Kumar and Bector (1991) reported 0.06% soluble nitrogen in laboratory made paneer. According to Haridas and Narayanan (1976) water soluble nitrogen and tyrosine content of fresh paneer was 0.18% and 9.21 mg/100g paneer respectively, however during storage with 0.4% formalin water soluble nitrogen and tyrosine content increased to 0.45% and 34.39 mg/100g paneer respectively after 21 days at room temperature. In present investigation also increase in the WSN content, tyrosine value and OPA content of 0.4% formalin preserved sample was an indication that this level of formalin is insufficient to kill all the microorganisms present in paneer and consequently due to their growth significant increase in these values was observed.
Figure 1: Acidity (% lactic acid) of control (a) and 0.4% formalin preserved paneer (b) during storage at 37°C

Figure 2: Water Soluble Nitrogen (WSN) of control (a) and 0.4% formalin preserved paneer (b) during storage at 37°C

Figure 3: OPA (µg L-Serine/g paneer) and Tyrosine content (mg/100g paneer) of control (a) and 0.4% formalin preserved paneer (b) during storage at 37°C

Figure 4: FFA (% oleic acid) of control (a) and 0.4% formalin preserved paneer (b) during storage at 37°C
Kumar and Bector (1991) reported 0.28% oleic acid FFA content in fresh paneer which increased to 0.5 on 22nd day of storage at 5 °C. Similar trend of FFA content was found in present study. An increase in the FFA value in 0.4% formalin preserved paneer is an indication that formalin may not able to inactivate lipase enzyme and was insufficient to kill all the microorganisms present in paneer that released microbial lipase. Both of these may contributed to lipolysis and therefore significant increase in FFA value was observed.

Boghra et al (1997) reported peroxide value (ml of 0.002 N Na₂S₂O₃/g) 0.0 in fresh paneer sample, which increased to 0.173 after 8 days at ≤10 °C. Thus, values for increase in peroxide value of paneer on storage obtained in present study are in general agreement with above reported study. During the storage increase in the peroxide value, conjugated diene and total carbonyl content was an indication that the auto-oxidation of unsaturated fatty acids has taken place. The extent of increase was directly proportional to the extent of auto-oxidation of fat. An increase in these values in 0.4% formalin preserved paneer is an indication that formalin may not provide protection against auto-oxidation. However, the values were comparatively less than control paneer samples.

Haridas and Narayanan (1976) reported that paneer sample could be preserved well in sterilized and stoppered glass bottles only for 6 days with the addition of formalin (0.4% v/w). Total period of analysis was 21 days, at 21st day, the samples became moldy and there was a decrease in fat and total nitrogen content and increase in water soluble nitrogen, tyrosine content and titratable acidity of the paneer.

**Conclusions**

From present investigation it can be concluded that changes in chemical characteristics of paneer were observed just after 1st month of storage. But after 2nd month of storage there was excess gas production and very foul smell due to growth of microorganisms.

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