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Keeping Quality of Ghee in Relation to its Copper Content

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ABSTRACT

The cream having 42% fat was pasteurised at 85°C for 20 seconds in which copper was added as copper sulphate solution at the rate of zero, 100, 200 and 500 μg./kg. The *ghee* was prepared by cream-butter-*ghee* process and stored at 6°C and room temperature. The keeping quality of *ghee* was studied for 20 weeks storage period by chemical tests like peroxide value, FFA content and TBA values. The copper content of *ghee* did not show any effect on development of FFA and TBA value but Peroxide value was observed to be in most accordance with the copper content of *ghee*.

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INTRODUCTION

Keeping quality of *ghee* is affected by several factors, among which copper plays an important role in deteriorating the *ghee* quality by oxidative reaction. The extra quantity of the copper could be detected in milk and milk products more than naturally present, could be due to insufficient care taken to prevent its contamination to milk and milk products from various sources like animal body surface including udder, hands of milker, milking pails, seives, processing equipments to which it comes in contact and packaging materials. Limited amount of work has been reported on effect of added or absorbed copper on *ghee* quality. Paul *et al.* (1949) observed them *ghee* stored in brass and bronze vessels showed highest peroxide value development than aluminium vessels and mud-pots. Al-Sokkary and Ghoneim (1952), Bector and Narayanan (1972) and Unnikrishnan and Rao (1977) had seen effects of contaminated copper on quality of *ghee* during storage and seen that induction period of *ghee* was significantly decreased with even minute contamination with copper.

MATERIALS AND METHODS

Pasteurized cream (heated to 85°C for 20 seconds and cooled to 4°C) was taken in 400 kg quantity for each trial. The cream was immediately analysed for acidity, fat and storch tests and found that fat (42.0 to 42.1%) acidity (0.08 to 0.09% L.A.) and Storch test (negative) was normal for five trials. The cream was divided into four batches each amounting to 100 kg. Copper was added to the cream as copper sulphate soultion (200 μg Cu/ml) at the rate of zero (Cu_0), 100 (Cu_1), 200 (Cu_2) and 500 (Cu_3) μg Cu/kg of cream. Butters were prepared from these copper treated cream in stainless steel butter churn. For the preparation of *ghee* ,butter sample of about 2 kg from each treatment, viz., Cu_0, Cu_1, Cu_2 and Cu_3 was used. The butter was prepared into *ghee* using the temperature of 115°C. The process of *ghee* making was considered complete when the *ghee* residue turned into light chocolate colour. All the containers

used for *ghee* making throughout the study were made of stainless steel. *Ghee* was filtered through muslin cloth and was packed brimfully in 60 ml screw capped bottles to remove air as far as possible. *Ghee* samples were stored at 6±1°C (T_2) and at room temperature (RT) for 20 weeks.

The samples of the *ghee* were tested during the storage period of 20 weeks at an interval of 5 weeks for Peroxide value (PeV), Free Fatty Acids (FFA) content and Thiobarbituric acid (TBA) value. PeV (m.eq./kg fat) of *ghee* was determined by the "Ferric Thiocyanate method" of Loftus-Hills and Theil (1946) modified by Holloway (1966). FFA content (% oleic acid) of *ghee* was determined as per the standard method prescribed by ISI (IS : 3508–1966). TBA test used for *ghee* was of El-Negoumy and Hammond (1962).

"Spectronic 20" (Bousch and Lomb, USA) was used to determine the optical density of colour developed in the PeV and TBA tests. Copper content of *ghee* was determined as per the standard method (colorimetry) prescribed by ISI) (IS : 3507–1966) and also by Atomic Absorption Spectrophotometry (AAS) (Atomic Absorprion Spectropeotometer, AA/120, Varion Techtron Co., Australia) at 3253, λ wavelength as per Willis (1964).

RESULTS AND DISCUSSION

Natural copper content of cream and *ghee* have been shown in Table 1. The mean of copper content in cream by colorimetry was 490 μg/kg while that of by AAS was 403 μg/kg. The mean of the natural copper content in *ghee* was 36 and 27 μg/kg by colorimetrically and AAS, respectively. The *ghee* prepared from cream added with Cu_1, Cu_2 Cu_3 and copper showed 46, 54 and 78 μg Cu/kg by colorimetry and 32, 41 and 69 μgCu/kg by AAS, respectively. The difference between copper content of *ghee* samples of different treatments was found to be significant indicating that addition of copper to cream results in to increased copper content of *ghee*.

Peroxide Value:

Peroxide values of ghee at 6°C:

The threshold PeV of all *ghee* samples stored at 6°C varied from 0.09 to 0.12. The PeV increased with the duration of storage period. The rate of increase of PeV was not similar in samples having different copper levels at 6°C. The peroxide development was highest, 0.12 to 1.40 in the *ghee* samples having Cu_3 level while it was lowest, 0.11 to 0.47 in samples having Cu_0 level at 6°C during 20 weeks of storage. Cu_1 level showed higher rate of peroxide development, 0.11 to 0.66 than Cu_0 level. This indicates that even at 6°C storage temperature, the addition of 100 μg Cu/kg (to cream) would cause appreciable deterioration of *ghee* even after 20 weeks storage period. Cu_2 level showed 0.09 to 0.85 development in PeV which was higher than Cu_1 level but when PeV development was compared with that of Cu_3 level, the Cu_3 level showed higher PeV compared to all other samples indicating significant role of copper in decreasing shelf life of *ghee*.

Peroxide values of ghee at room temperature:

The threshold values of all *ghee* samples varied from 0.09 to 0.12. The PeV increased with the duration of storage period. The rate of development of PeV was not similar in samples having different copper levels at RT. The PeV was highest, 0.12 to 6.52 in *ghee* samples having Cu_3 level while it was lowest, 0.11 to 1.92 in samples

having Cu_0 level at RT during 20 weeks storage. The overall rate of PeV development was increased with the increase of copper content in *ghee* samples. Cu_1 level showed higher rate of Pev development, 0.11 to 2.26 than Cu_0 level. Cu_2 level showed 0.09 to 3.10 PeV development in 20 weeks storage.

Effect of Storage temperature on PeV of Ghee:

Storage temperature showed definite effect on keeping quality of *ghee* as indicated by PeV of *ghee* samples. All samples stored at 6°C showed lower PeV development than the samples stored at RT. The *ghee* samples having Cu_0 level at RT showed even high PeV development, 0.11 to 1.92 than the PeV development, 0.12 to 1.40 in *ghee* samples having Cu_3 level at 6°C during twenty weeks storage. Overall, the rate of development of PeV was proportional to copper content of *ghee* samles at each temperature but the rate of increase was higher at RT than 6°C. This indicates that the copper plays an important catalytic role in deterioration of *ghee* samples stored at higher temperature. While this effect can be minimized by storing the *ghee* samples at low storage temperature.

Paul *et al.* (1949) recorded highest PeV in *ghee* stored in brass and bronze containers compared to glass and aluminium containers. They concluded that catalytic action of copper was probably responsible for high PeV during storage. Bector and Narayanan (1972) observed that various levels, zero, 0.1 and 1.0 ppm copper added to clarified butter fat and considerable effect on PeV development and PeV increased from 0.00 to 6, 9 and 15 m. eq./kg fat respectively when butter fat was stored at 80° C for 96 hours. They concluded that copper catalysed the oxidation of butter fat and decreased the induction period of butter fat considerably with higher amounts of added copper. Similar observations were made by Unnikrishnan and Rao (1977) that with the increase in copper content of *ghee*, the PeV was also increased during storage at 25° C. They observed 0.17 PeV for control samples and 1.00 PeV for samples in which 0.1 ppm of copper was added, the samples were stored at 25° C for 14 weeks. Al-Sokkary and Ghoneim (1952) studied the effect of addition of copper sulphate solution to butter on keeping quality of samna at 5°C and 40°C. They observed resultant samna contained 0.0 to 25 ppm copper and the PeV of samna samples were proportional to their copper content at both, 5°C and 40°C storage temperatures. They concluded that even minute proportions of copper were capable of producing very objectionable changes in samna.

Free Fatty Acids (FFA) Contents (% Oleic Acid):

FFA Content of Ghee at 6°C:

The threshold FFA content of *ghee* samples varied from 0.150 to 0.156%. The FFA content of *ghee* samples increased from 0.150 to 0.192 for all treatments samples after 20 weeks storage period.

FFA content of Ghee at Room Temperature:

The FFA content of freshly made *ghee* samples varied from 0.150 to 0.156%. After 20 weeks storage period, these levels increased to 0.294 to 0.300 in all samples of *ghee* stored at RT which could be considered as two-fold increase in FFA content of *ghee* stored

at RT. The addition of copper at any level did not show any effect on FFA development in *ghee* samples.

Effect of Storage Temperature on FFA Content of Ghee:

The rate of increase of FFA content in *ghee* was higher at RT than at 6°C. The values for FFA content of *ghee* after 20 weeks storage period ranged from 0.294 to 0.300% and 0.190 to 0.192% at RT and 6°C, respectively.

Paul *et al.* (1949) observed slight increase in FFA content of *ghee* during 24 weeks storage period. The increase was from 0.20 to 0.28%. Gaba and Jain (1975) also have reported similar findings that during 100 days of storage, FFA content of *ghee* increased from 0.24 to 0.34%. Singh and Ram (1978) also found two-fold increase in FFA at ten months storage period. The results of the present experiment are in agreement with the research work reported by other scientists.

The copper content of different *ghee* samples did not show any effect on FFA development at both the storage temperatures, indicating no effect of copper content on FFA development of *ghee*. Rangappa and Achaya (1974) reported that pro-oxidant metals like Cu and Fe did not cause hydrolysis of *ghee*, but caused the autoxidation of *ghee*.

Thiobarbituric Acid (TBA) Value:

TBA Values of Ghee at 6°C:

The threshold TBA values of all *ghee* samples varied from 0.34 to 0.35. Initially there was not much difference in TBA values of *ghee* samples. As the storage period increased, the TBA values showed no definite trend. At the end of 5 weeks, TBA values were decreased, ranging from 0.18 to 0.24. The TBA values were increased at the end of 10 weeks, ranging from 0.22 to 0.43. The TBA values were again decreased at the end of 15 weeks, ranging from 0.13 to 0.30 and again increased at the end of 20 weeks, ranging from 0.31 to 0.56. Storage period did not show any definite change in TBA values. However, the copper content of *ghee* had an appreciable effect on TBA values of *ghee*. The TBA values were increased at definite storage period, when copper content of *ghee* samples increased. Cu_0 level samples of *ghee* showed 0.18, 0.22, 0.13 and 0.31 and Cu_3 level showed 0.24, 0.43, 0.30 and 0.56 TBA values at the end of 5, 10, 15 and 20 weeks storage period, respectively.

TBA Values of Ghee at Room Temperature:

The threshold TBA values of *ghee* were same as that of *ghee* at 6°C. As storage period increased the TBA values showed fluctuations and showed inconsistent relation to storage period. The TBA values ranged from 0.22 to 0.31, 0.23 to 0.75, 0.16 to 0.37 and 0.38 to 1.06 at the end of 5, 10, 15 and 20 weeks storage periods, respectively. Considering the effect of copper content on TBA values of *ghee* samples stored at RT, it was significant. As the copper content of *ghee* samples increased, the TBA values also increased and the highest TBA values were noticed in samples having Cu_3 level at RT and lowest was in samples having Cu_0 level at RT.

Effect of Storage Temperature on TBA Values of Ghee:

Storage temperature showed definite effect on TBA values of *ghee*. The TBA values were lower at 6°C than RT in *ghee* samples having same copper levels. The TBA values were highest in Cu_3 level *ghee* samples at each storage period levels while they were

lowest in samples having Cu_0 level. The TBA values at Cu_1 level were higher than Cu_0 level but definitely lower than Cu_2 level at both storage temperatures.

Singh and Ram (1978) found that the TBA value of *ghee* showed erratic fluctuations during storage period of ten months while Gaba and Jain (1975) reported steady increase in TBA values of *ghee* during storage. Hamm *et al.* (1968) reported that samples stored at low storage temperature gave lower TBA values of butter fat than higher storage temperature. They also observed that butter fat containing higher copper showed higher TBA values during storage.

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TABLE 1

Copper content of cream and ghee (μg/kg) as affected by addition of copper to cream and method of analysis (Mean of five replications).

Cream		*Copper added to cream*	*Ghee*	
Colorimetry	*AAS*		*Colorimetry*	*AAS*
		—	36	27
490	403	100	46	32
		200	54	41
		500	78	69

TABLE 2

Peroxide value (m.eq./kg fat) of ghee as affected by copper content, storage temperature and storage period (Mean of five replications).

Storage period	*Storage Temperature*							
	$6° \pm 1°C$ (T_2)				(RT)			
	Copper treatment to cream							
	Cu_0	Cu_1	Cu_2	Cu_3	Cu_0	Cu_1	Cu_2	Cu_3
S_0	0.11	0.11	0.09	0.12	0.11	0.11	0.09	0.12
S_1	0.16	0.18	0.20	0.20	0.31	0.34	0.35	0.53
S_2	0.23	0.24	0.24	0.38	0.77	0.77	1.06	1.42
S_3	0.34	0.34	0.47	0.83	1.32	1.68	1.94	3.36
S_4	0.47	0.66	0.85	1.40	1.92	2.26	3.10	6.52

TABLE 3

Free fatty acids content (%oleic acid) of gree as affected by copper content, storage temperature and storage period (Mean of five replications).

Storage period	Storage Temperature							
	$6°\pm1°C$ (T_2)				RT			
	Coper treatment to cream							
	Cu_0	Cu_1	Cu_2	Cu_3	Cu_0	Cu_1	Cu_2	Cu_3
S_0	0.154	0.156	0.156	0.150	0.154	0.156	0.156	0.150
S_1	0.158	0.160	0.160	0.158	0.172	0.174	0.174	0.176
S_2	0.170	0.174	0.168	0.170	0.212	0.212	0.214	0.216
S_3	0.180	0.178	0.186	0.174	0.254	0.256	0.248	0.240
S_4	0.190	0.192	0.192	0.190	0.294	0.298	0.296	0.300

TABLE 4

TBA value of ghee as affected by copper content, storage temperature and storage period (Mean of five replications).

Storage period	Storage Temperature							
	$6°\pm1°C$ (T_2)				RT			
	Copper treatment to cream							
	Cu_0	Cu_1	Cu_2	Cu_3	Cu_0	Cu_1	Cu_2	Cu_3
S_0	0.35	0.34	0.34	0.35	0.35	0.34	0.34	0.35
S_1	0.18	0.19	0.21	0.24	0.22	0.24	0.25	0.31
S_2	0.22	0.28	0.36	0.43	0.23	0.40	0.55	0.75
S_3	0.13	0.17	0.22	0.30	0.16	0.20	0.32	0.37
S_4	0.31	0.38	0.47	9.56	0.38	0.62	0.79	1.06

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