EFFECT OF CERTAIN CHEMICAL PRESERVATIVES ON THE PHYSICO- CHEMICAL PROPERTIES OF COW AND BUFFALO MILK

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ABSTRACT

The efficiency of milk sample preservatives such as Formalin-0.4%, Potassium dichromate-0.4% and Bronopol (2-Bromo-2Nitro-1, 3 Propanediol)-0.1% was compared. Cow and buffalo milk samples could be preserved up to 90, 30 days with the addition of formalin and potassium dichromate respectively. Bronopol treated cow and buffalo milk samples could be preserved for 24, 16 days respectively. Significant difference was noticed in titratable acidity and pH of the preserved samples when compared to control ($P<0.05$). None of the three preservatives had significant effect on fat, solids-not fat and total solids contents by standard methods. However, samples preserved with potassium dichromate showed significant decline in fat percentage by electronic Milko-tester.

Key words: Bronopol, Formalin, Milk sample preservatives, Potassium Dichromate

INTRODUCTION

In India, as per the Prevention of Food Adulteration Act (1954), addition of 0.4 per cent formalin has been legally permitted for the preservation of milk samples intended for chemical analysis in quality control laboratories. Effect of formalin on Gerber fat test has been a controversial subject in the recent past. Recently, many other chemicals like potassium dichromate, sodium azide and bronopol have been studied as milk sample preservatives in India and abroad. However, there is no authentic and comparative information available in this regard. Hence, the present investigation was undertaken to assess the effect of different chemical preservatives such as formalin, potassium dichromate and bronopol on major milk constituents in cow and buffalo milk samples.

MATERIALS AND METHODS

Pooled milk samples were collected from cows and buffaloes maintained at University Livestock Farm. Samples were divided into three parts and preserved with formalin-0.4%, potassium dichromate-0.4% and bronopol (2-Bromo-2-Nitro-1, 3 Propanediol)-0.1% separately to study the duration of preservation at room temperature and also to study the effect on major milk constituents. After the addition of preservatives, milk samples were closed tightly and kept at room temperature. Milk samples were analyzed for pH (Electronic pH Meter), titratable acidity, fat (Gerber and Milko-Tester), total solids (Gravimetric) and solids-not-fat (by difference] at zeroth and last day of storage. Before each analysis milk samples were shaken well and warmed to 40°C for 5 minutes and cooled down to 27°C. Data were analyzed by using analysis of variance test (Snedecor and Cochran, 1989).

RESULTS AND DISCUSSION

The mean values with standard error of different parameters in cow and buffalo milk samples preserved with three preservatives are presented in the Table.1. Formalin added cow and buffalo milk samples could be preserved up to 90 days without curdling and colour change at room temperature. Potassium dichromate treated samples became orange in colour immediately on addition of potassium dichromate and changed to green in colour at the latter stage. They showed signs of curdling from 30 th day onwards. Bronopol added cow and buffalo milk samples could be preserved up to 24 and 16 days respectively and they became pink in colour with signs of curdling at the final stage of storage. Similar observations were reported by Bansal (1989), Jandal and Rai (1989), Bajaj and Rai (1992) in formalin and Kroger (1985) Desraj and Singhal (1996) in potassium dichromate treated milk samples. In bronopol treated samples, 10-14 days of storage life was reported at room temperature with 0.02% bronopol (Gencurova *et al*., 1995). However, in the present study 0.1% concentration was used, this might be the reason for relatively longer period of storage. The colour change in potassium dichromate preserved samples might be due to reduction of orange hexavalent chromium anion in the chromate to the trivalent chromium ion, likely caused by reducing bacteria. But in bronopol preserved milk samples the reason was not clear.

pH

The mean pH values on zero th day of storage in cow milk samples preserved by formalin, potassium dichromate and bronopol were 6.46±0.01, 6.19±0.02 and 6.56±0.03 respectively. The corresponding values for buffalo milk samples were 6.58±0.03, 6.27±0.01 and 6.72±0.01 respectively. A sudden drop in pH was noticed in potassium dichromate treated samples whereas, the fall in pH was moderate in formalin and less in bronopol preserved samples. However, an increase in pH was noticed in potassium dichromate treated cow and buffalo milk samples at the final stage of storage, in contrast to low pH in formalin and bronopol added samples. Decrease of pH in formalin preserved samples may be due to low pH of formalin and its reaction with milk protein at later stage (Jandal and Rai, 1989). The change in pH was significant ($P<0.05$).

Titratable Acidity

The mean titratable acidity on zero th day of storage in cow milk samples preserved by formalin, potassium dichromate and bronopol were 0.20±0.01, 0.38±0.01 and 0.18±0.01 respectively. The corresponding values for buffalo milk samples were 0.18±0.01, 0.36±0.01 and 0.16±0.00 respectively. A sudden significant rise in titratable acidity was noticed on addition of potassium dichromate, but the values decreased at the final stage of storage. Formalin and bronopol added samples showed a moderate and consistent increase in titratable acidity. Karmakar and Ghatak (1997) reported similar findings in milk samples preserved with formalin. The initial increase of titratable acidity in formalin preserved samples may be due to its acidic nature and proteolytic activity in later stages (Bansal and Singhal, 1991; Karmakar and Ghatak, 1997). The increase in titratable acidity was significant ($P<0.05$).

Fat Percentage

The mean fat% on zero th day of storage in cow milk samples were 3.32±0.10, 3.40±0.01 and 3.42±0.09 for formalin, potassium dichromate and bronopol treated samples respectively. The corresponding values for buffalo milk samples were 6.13±0.22, 6.20±0.22 and 6.21±0.19 respectively.

None of the three preservatives had significant effect on fat. However, a slight decrease was noticed in potassium dichromate preserved samples and this may be attributed to the degradation of milk fat by the strong

oxidative property of the chemical (Desraj and singhal, 1990). Monardes *et al.* (1995) reported that milk preserved with potassium dichromate had lower fat and protein percentages than those preserved with bronopol. Radha *et al.* (2004) reported that bronopol had no influence on fat percentage by Gerber's method. Several authors have reported a significant decrease in fat% in formalin preserved samples under standard Gerber method. But in the present study a modified Gerber method was used by increasing the sulphuric acid concentration to 94% to dissolve milk solids completely.

Fat Percentage (Milko-tester)

The mean fat% on zeroth day of storage in cow milk samples were 3.33±0.10, 3.38±0.10 and 3.45±0.01 for formalin, potassium dichromate and bronopol treated samples respectively. The corresponding values for buffalo milk samples were 6.13±0.21, 6.20±0.22 and 6.22±0.19 respectively.

A significant decrease in fat% was noticed in potassium dichromate preserved samples and the results are in agreement with the reports made by Kroger (1985). This may be due to changes in the physical structure due to aging of milk samples. In bronopol preserved cow and buffalo milk samples a slight but non significant increase in fat percentage was noticed.

The slight decrease in fat % in formalin preserved samples may be due to fat globule membrane damage caused by the reaction of formalin with proteins which result in reduction of number as well as surface area of fat globules (Bansal, 1989). Use of Milko-tester for the estimation of fat in the formalin preserved samples was reported unsatisfactory by many workers (Bansal, 1989; Bajaj and Rai, 1992). Sesķena and Jankevica (2007) reported that there were no considerable changes in fat content in the samples treated with sodium azide, bronopol, potassium sorbate, and azidiol at 4 °C and 20 °C.

Solids-not-fat

The mean solids not fat% on zeroth day of storage in cow milk samples were 9.14±0.02,

Table.1. Mean (±SE) values of different parameters in cow and buffalo milk samples preserved with chemical preservatives

Parameters	Species	Control	Formalin		Potassium dichromate		Bronopol	
			0 day	Last day	0 day	Last day	0 day	Last
pH	Cow	6.58±0.02	6.46±0.01	6.06±0.02	6.19±0.02^{b}	6.42±0.02^{b}	6.56±0.03	6.04±
	Buffalo	6.76±0.01^{a}	6.58±0.03	6.21±0.01^{b}	6.27±0.01^{b}	6.44±0.02^{b}	6.72±0.01	6.18±
Titratable acidity	Cow	0.16±0.01^{a}	0.20±0.01	0.27±0.00^{b}	0.38±0.01^{b}	0.28±0.01^{b}	0.18±0.01	0.29±
	Buffalo	0.13±0.00^{a}	0.18±0.01	0.25±0.00^{b}	0.36±0.01^{b}	0.28±0.01^{b}	0.16±0.00	0.25±
Fat (%) (Gerber)	Cow	3.40±0.09	3.32±0.10	3.38±0.00	3.40±0.01	3.34±0.09	3.42±0.09	3.42±
	Buffalo	6.20±0.22	6.13±0.22	6.18±0.22	6.20±0.22	6.13±0.21	6.21±0.19	6.25±
Fat (%) (Milko-tester)	Cow	3.40±0.09	3.33±0.10	3.43±0.02	3.38±0.10	3.25±0.10	3.45±0.01	3.44±
	Buffalo	6.20±0.22^{a}	6.13±0.21	6.32±0.34	6.20±0.22	5.77±0.21^{b}	6.22±0.19	6.25±
SNF%	Cow	9.05±0.10	9.14±0.02	9.12±0.10	9.10±0.18	9.19±0.13	9.02±0.10	9.03±
	Buffalo	9.42±0.27	9.45±0.29	9.41±0.28	9.46±0.27	9.58±0.27	9.44±0.26	9.43±
Total solids%	Cow	12.45±0.12	12.46±0.13	12.50±0.10	12.50±0.13	12.54±0.14	12.47±0.10	12.48
	Buffalo	15.62±0.48	15.58±0.49	15.59±0.49	15.66±0.48	15.70±0.48	15.66±0.46	15.69
Duration of storage	Cow	90			30		24	
	Buffalo	90			30		16	

*n = 6

*ab = means bearing different superscripts within the same row differ significantly (P>0.05)

9.10±0.18 and 9.02±0.10 for formalin, potassium dichromate and bronopol treated samples respectively. The corresponding values for buffalo milk samples were 9.45±0.29, 9.46±0.27 and 9.44±0.26. No significant change was caused by the three preservatives studied. However, potassium dichromate caused a slight increase in SNF content. This may be attributed to the solid nature of the preservative. Many previous studies have also shown similar findings in formalin (Jandal and Rai, 1989) preserved samples. Nitima *et al*. (2004) have reported that bronopol and potassium dichromate had slightly altered the fat, lactose, protein content by infrared Spectrophotometric method.

Total Solids

The mean total solids % on zeroth day of storage in cow milk samples were 12.46±0.13, 12.50±0.13 and 12.47±0.10 for formalin, potassium dichromate and bronopol treated samples respectively. The corresponding values for buffalo milk samples were 15.58±0.49, 15.66±0.48 and 15.66±0.46. No significant change in total solids content was noticed except a slight increase in potassium dichromate added samples. This is in agreement with reports made by Bansal (1989); Bajaj and Rai, (1992). As the level of preservative added was very low, it might not have added any measurable weight to the sample.

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