DETERMINING CLEANLINESS OF MILK CONTACT SURFACES BY ANALYZING FOR CALCIUM RESIDUAL: PRELIMINARY STUDIES[1]

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SUMMARY

A new procedure for determining cleanliness of milk processing equipment is discussed. Calcium was removed from milk-contact surfaces by applications of 1 M HCl and scraping with a plastic spatula. Quantities removed were determined by atomic absorption spectroscopy. The mean residual concentration of calcium on equipment after "control cleaning" was equivalent to 0.07 mg/100 cm², and 95% confidence limits indicated insufficient cleaning if the residual was 0.08 mg/100 cm² or higher. Suggestions for improving the method are included.

Methods for determining cleanliness of milk processing equipment have previously been based on recovery of microorganisms *(1)*, use of radioactive isotope tracers *(3)*, inactivation of hypochlorite by soil *(4)* and miscellaneous methods. Disadvantages of these methods are many and varied ranging from poor repeatability to extreme complexity. We were seeking a simple, reproducible method that could be applied industrially and in research.

Our hypothesis for study stated that since calcium is a major constituent of milk, of milkstone, and presumably of the majority of films left on milk processing equipment, quantitative removal and analysis of calcium from milk films would produce a reliable measurement of equipment cleanliness. Highly sensitive and relatively rapid quantitative tests are now available for calcium. We theorized that quantitative removal of calcium could be achieved by thorough washing of the sample surface using a strong acid.

MATERIALS AND METHODS

Applications of milk films. Skimmilk was applied to the tank walls using a sanitizer fogging device. The droplets were allowed to collect until the film just started to flow down the walls. The film was then allowed to become visibly dry prior to analyses or the rinse or wash experiments.

Rinse and wash procedures. Cleaning was done with an automatically controlled CIP spray ball system mounted in a rectangular 2500 gal. insulated storage tank. The single spray ball was mounted in the center of the tank which measured 5' x 9' x 11'. The cycle provided for a 3 min rinse with tap water at 32 C, a 9 min detergent wash at the specified temperature and a 2 min cold water rinse.

Detergent evaluations. Preliminary trials were made to determine the applicability of this method for evaluating efficiency of cleaning by cold water detergents. Detergents tested were as follows: AIM, a bulk milk-tank cleaner (A); 2214, an experimental formulation by Economics Laboratories (B); and Klenz-mate formula 2124, a liquid mechanical dishwasher detergent (C).

Template. A frame (Figure 1) made of extruded aluminum alloy was welded and coated with epoxy paint (O-Brien Mira-Plate) to preclude corrosion. A gasket made of silicone rubber (Dow-Corning) was formed around the bottom of the template to prevent sample escape and facilitate recovery of test solutions. The handle was constructed to provide even pressure distribution on the gasket.

Calcium removal. The 440 cm² sample area formed by the template was flushed with 10 ml portions of 1 M HCl and distilled water. Dry milk films were removed by 2 applications of water, 3 of acid, and 1 of water; whereas, after rinsing or washing, the order of application was acid, acid, water, acid, water, water. It was necessary to first apply water to the heavy milk film to prevent excessive protein coagulation. Solvent applications were made using a glass syringe, and the area was scraped between flushings with a plastic spatula moving from upper right to lower left (Figure 1). This loosened the film and swept the solution from the surface. Samples were collected in plastic milk sample bags which were tied beneath the template.

Each wall of the tank was sampled after performance of the treatment being tested. Thus, 4 samples were available for analysis from each trial. When a series of different treatments was necessary, samples were taken from adjacent areas so no overlap of sampling areas occurred. Duplicate determinations were made of calcium content of each sample.

To evaluate the sample collection method, 3 series of 8 consecutive applications of 10 ml acid were made. With 1 exception each 10 ml portion was collected separately and analyzed for calcium content to determine at what point residual calcium reached a level equivalent to that in the

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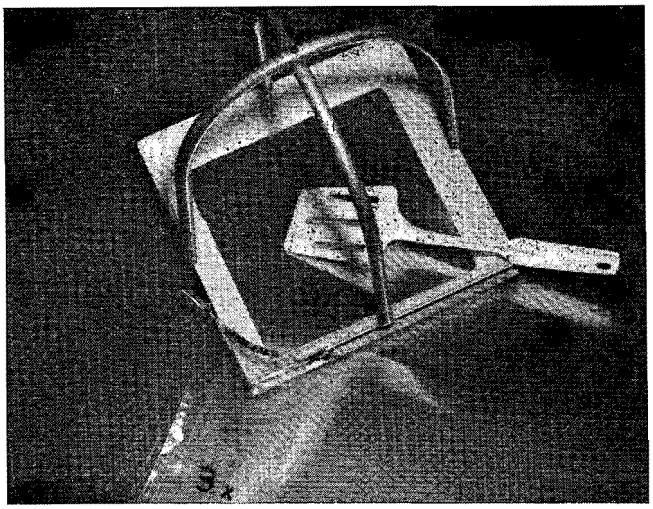

Figure 1. Template constructed of aluminum alloy coated with epoxy paint. The area within the silicone rubber gasket is 440 cm². The spatula and sample bag are made of plastic.

acid rinse solution (0.2 ppm).

To avoid film buildup, and possible interactions between treatments, "control cleaning" was used after a treatment or treatment series was completed. This consisted of consecutive applications for 15 min each of alkaline (Klenzade HC-41 at 66 C) and acid (Klenzade AC-3 at 60 C) detergents, respectively. This was followed by a 3 min rinse with tap water.

Because tap water contained about 15 ppm. calcium, surfaces were rinsed with distilled water before sampling to remove traces of tap water. Preliminary experiments indicated this to be essential.

Calcium analyses. Atomic absorption spectroscopy was used (2, 5). To a 10 ml volumetric flask was added 8 ml sample, 0.5 ml of 2% lanthanum solution (5) and deionized-distilled water to bring to volume. Only 4 ml of sample were used when a highly soiled surface was sampled.

Concentrations of calcium in the standards were representative of the samples, and a control containing no added calcium was prepared. A standard curve was plotted from which sample calcium concentrations were determined.

Analyses were performed on a Perkin-Elmer 290 atomic absorption spectrometer equipped with a zinc and calcium lamp and a strip chart recorder. Acetylene was the fuel gas and filtered compressed air the supporting gas.

RESULTS AND DISCUSSION

Removal of calcium from the milk film was essentially complete after the third application of 10 ml of acid (Figure 2) when either highly or slightly soiled walls were tested. When the surface was heavily soiled, samples 1 and 2 were collected together and this value was plotted in the intermediate position. Quantities of calcium in control samples of acid are represented by the horizontal dotted line. Three applications of acid resulted in practically quantitative calcium removal.

When a surface was heavily soiled, protein coagulation resulted when acid was applied making the soil difficult to remove. This could be avoided by first applying 10 ml water and collecting the sample with the aid of the spatula. This should be considered in establishing a standard procedure.

Data in Table 1 represent 4 determinations each, 1 sample from each tank wall, for the various test conditions. Trials evaluating the "control-wash" and the "after rinse" residual were replicated 4 times (4 tanks-4 samples per tank). Others were duplicated (2 tanks-4 samples per tank). The mean calcium concentration after control cleaning was 0.5 ppm. which is equivalent to 0.07 mg/100 cm². Ninety-five per cent confidence limits placed the true mean within the range 0.214-0.786 ppm. Therefore, it should be valid to consider concentrations of 0.8 ppm (0.11 mg/100 cm²) and higher as indicative of excessive milk residual if the control wash was satisfactory. Such an interpretation indicated that none of our experimental detergent/temperature combinations were completely effective. However, detergent A (66 C) in trial 2 and detergent B (35 C) in trial 1 produced good results. In other instances one or more areas were "acceptably" clean but not all areas. Twice we observed "acceptable" residual after only rinsing. The relatively large amount of calcium removed by the rinse procedure is noteworthy. We had expected greater differences in quantities of calcium removed from the rinsed surfaces and the washed surfaces.

Variations in cleanability of the tank walls probably influenced these data. Visual observations in-

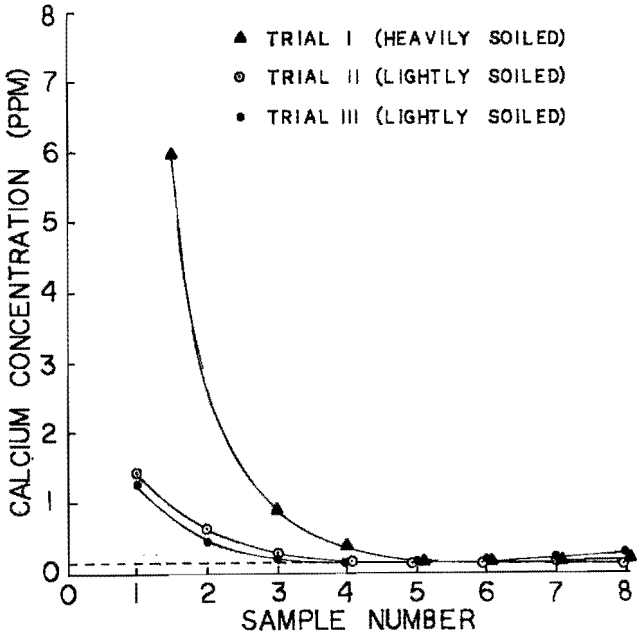

Figure 2. Parts per million of calcium in solutions taken in consecutive samplings of soiled milk-contact surfaces using 10 ml of 1 M HCl per sample.

TABLE 1. PARTS PER MILLION OF CALCIUM IN 60 ML OF SOLUTION USED TO REMOVE CALCIUM FROM 440 CM^2 TEST AREA AFTER VARIOUS TREATMENTS OF THE SOILED SURFACES

Trial No.	Control Wash	Dry Milk Film	After Rinse (32 C)	Detergent A (66 C)	Detergent A (35 C)	Detergent B (35 C)	Detergent C (35 C)
1	0.5	8.3	2.0	1.0	1.3	0.4	1.1
	0.4	7.2	2.0	0.7	0.9	0.5	1.0
	0.3	7.8	0.6	0.9	0.9	0.7	0.9
	0.4	6.3	1.2	0.8	0.8	0.5	1.0
Trial mean	0.4	7.4	1.4	0.8	1.0	0.5	1.0
2	0.8	10.3	1.5	0.6	0.6	1.0	1.9
	0.3	9.4	1.6	0.4	0.5	0.6	0.6
	0.4	9.0	0.9	0.6	0.7	0.6	0.7
	0.4	8.4	1.0	0.4	1.0	1.0	0.6
Trial mean	0.5	9.3	1.2	0.5	0.7	0.8	0.9
3	0.6		1.9				
	0.5		1.7				
	0.6		1.6				
	0.7		1.9				
Trial mean	0.6		1.8				
4	0.6		1.4				
	0.5		1.4				
	0.5		1.4				
	0.5		0.6				
Trial mean	0.5		1.2				
Treatment mean	0.5	8.3	1.4	0.6	0.8	0.6	1.0

dicated considerable differences in velocity of water runoff from tank walls.

Use of the confidence limits in interpreting these results provides an objective measurement of cleanliness. Our visual observations indicated a well-cleaned tank after the "control cleaning". Also recognized is the probability that some calcium will be found in samples from acceptably clean surfaces because of residual from tap water. However, we anticipate that the confidence interval can be reduced by procedural modifications.

A potential source of error is leakage around the template gasket. During our latter experiments, samples were weighed to assure recovery of essentially all the acid and water. Since we did not weigh them during earlier studies, this could have been the cause of some variation. The template gasket was flexible but not sufficiently so to allow sampling from curved or very uneven surfaces.

These results constitute a preliminary report of a method considered potentially quite useful. Refinements and standardization of procedure will be necessary. The following are suggested: (*a*) reduce the quantity of calcium solvent to 25-30 ml, applying in 5 ml increments; (*b*) incorporate a non-ionic wetting agent in the solvent; and (*c*) allow buildup of film during evaluation of cleaners rather than stripping the walls clean after each trial. Such procedural changes will increase differences in calcium concentrations between control samples and those from incompletely cleaned surfaces.

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