MEMO

DATE: 30 July 2014

TO: National Organic Standards Board

FROM: Ecolab R&D

CC: Steve Pasek, Joe Morelli, Jim Winter, Jason Koerth

SUBJECT: Chlorite Residues in Milk

Chlorite residues in milk while using acidified sodium chlorite teat dips have not been a concern because chlorite residues were non-detectable in extended herd studies, and chlorite is not persistent in milk changing to chloride (Cl^-) that is already present in milk.

Residue Herd Study

Cornell University: Study 36039A0.004 (October 1989) Study Director: D.N. Galton

In a twelve week study, 10 lactating cows were dipped before and after each milking with an acidified sodium chlorite solution comprising 1.32% lactic acid and 3200 ppm sodium chlorite (4XLA®, Ecolab). Milk samples were collected during the baseline period, after 2, 4, and 6 weeks of product usage, and 2 weeks post treatment. Samples were collected and stored between 2-6^oC and analyzed for chlorite within 48 hours of collection. Milk samples were analyzed using high performance liquid chromatography (ion chromatography) with a limit of detection of 0.075 ppm. Results for all samples were below the limit of detection. Teat dip usage was monitored with an average of 3.7g/cow/application.

Chlorite in Milk

Challenges for Validating a Method of Quantifying Low Levels of Chlorite in Milk, Joseph Morelli, Cayce Warf, Maura Aldrich, Susan Woo, Proceedings of the National Mastitis Council Annual Meeting (2003), p 334.

An improved methodology for detecting chlorite in milk was explored based on US EPA Method 317.0 comprising the use of high performance liquid chromatography (ion chromatography) and a post column chromogenic reagent for UV/Vis detection. The method enabled limits of detection as low as 25 ng/ml based on standard solutions. However, rapid degradation of chlorite was observed in milk. Milk samples spiked with as much as 500 ppm chlorite showed no measureable chlorite within 24 hours. Chlorite degrades as an oxidant to chloride (Cl^-) which is common in milk.

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DATE: 30 July 2014

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CC: Joe Morelli, Jim Winter, Jason Koerth

SUBJECT: Workplace Exposure to Chlorine Dioxide Generated During Dairy Farm Teat Dip Application

Chlorine dioxide is a water soluble gas that has an odor similar to that of chlorine. It is an oxidizer and has been used as an antimicrobial for various applications. One such application has been the use in teat dips for approximately the last 25 years. One method to generate chlorine dioxide is by acidifying a sodium chlorite solution. The mechanism of acidification of a dilute sodium chlorite solution with a lactic acid based "activator" will serve as the basis for the following discussion.

OSHA permits up to 0.1 ppm (0.3 mg/m^3) of chlorine dioxide for an 8 hour time weighted average and 0.3 ppm (0.9 mg/m^3) of chlorine dioxide for a short term exposure limit. On farm testing was performed in order to determine the chlorine dioxide exposure levels generated using an Ecolab acidified sodium chlorite teat dip 4XLA.

A farm using a double 5 herringbone parlor with a room size of 125 m^3 and a milking pit depth of 1 m was selected for trial. The 4XLA Activator (acid component) was mixed with the 4XLA Base ($NaClO_2$ component) as directed per the label. The activated 4XLA was applied as a post dip using a manual spray device. 4XLA is not labeled for spray application use. However, for the sake of this trial we felt that a spray application would yield a worst case scenario as more chlorine dioxide gas should be released to the atmosphere due to the larger solution/atmosphere surface interface ratio. Two Dräger detection devices were used during testing. The first (Device 1 – see graph) was placed on the milker's back with the intake of the device placed near the respiratory tract of the milker. The second (Device 2 – see graph) was placed in the parlor pit, 50 cm from the floor. A minimum and maximum exposure threshold of 0.1 ppm ClO_2 and 0.2 ppm ClO_2 were selected for on farm testing and are shown as red lines on the graphs below.

Extension of Dräger device in daypack

The first test run was performed using a “normal” amount of teat dip (~4 g/cow). No (0 ppm) ClO_2 was detected with the Dräger detection device on the milker or in the pit during the first recording. A second and third test measurement was performed with the milker spraying twice the normal levels of teat dip (~8 g/cow). Again, 0 ppm ClO_2 was detected using both Dräger devices. The Dräger device inlet was placed directly into the headspace of a bottle of activated 4XLA. The peaks shown after milking on the graphs for the second and third run verify that the device was working properly. It should be noted that the Dräger device intake had to be within 10 cm of the sprayed product to exceed the detection limit.

This on farm study looking at three separate milkings has shown workplace exposure levels of 0 ppm ClO_2 using 4XLA as a manually spray applied post dip.

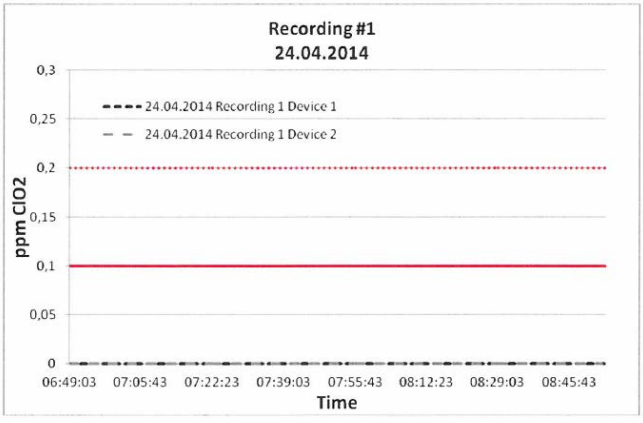

Figure 11: First measurement. No recorded ClO_2. Function test performed in laboratory. Device worked correctly

Note: Time Units (hh:mm)

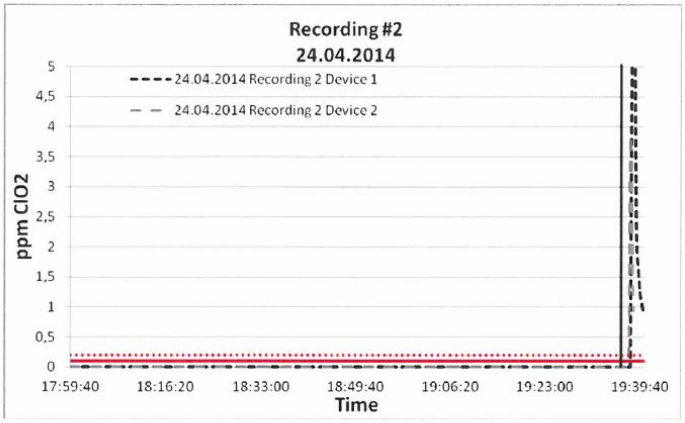

Figure 12: Second measurement. No recorded ClO_2 during milking. High peaks result come from function test after milking to show that device is working correctly. Black vertical line shows end of milking

Note: Time Units (hh:mm)

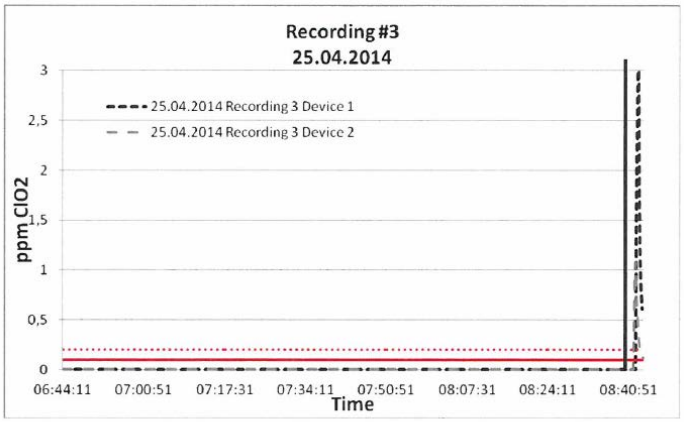

Figure 13: Third measurement. No recorded ClO_2 during milking. High peaks come from function test after milking to show that device is working correctly. Black vertical line shows end of milking

Note: Time Units (hh:mm)

If the concern is inhalation at mixing, there can be a low level of ClO_2 produced when the Activator (lactic acid) comes in contact with the Base (sodium chlorite) but the risk of measuring appreciable amounts is quite low. However, there is a finite amount that can be smelled that is helped by “convection” of air stirring things around. In this study we have a government authority defining safe exposure limits. Testing was carried out that very specifically looks at individual inhalation exposure under spray conditions that would be a worst case scenario and ClO_2 levels were well below the threshold. Knowing the level of ClO2 in the teat dip solution is separate than knowing the environmental exposure. Human sense of smell can pick up minute levels of many chemicals, so smelling an odor doesn’t mean that it is above a safe level. In this study the detection device had to be within four inches of the product to exceed the detection limit. When mixing a teat dip into a teat dip cup or a holding jug the mixed product would be at approximately an arm’s length from the face of the individual doing the mixing.