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Results from portable and of low cost equipment developed for detection of milk adulterations

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Abstract

This work presents the results of a device, MilkTech, developed to detect milk tampering, based on electrical measurements. The device indicates possible frauds by water, sodium chloride, caustic soda, ethyl alcohol and sodium bicarbonate. The advantages in relation to traditional methods are portability, low cost and detection of mixed frauds. The experiments were conducted in dairy plants at Governador Valadares, in Brazil. The results were compared with cryoscopy and chloride tests. It is demonstrated there is high correlation between MilkTech and Cryoscopy. For instance, the detection limit of the equipment for water addition with the set of analyzed data was 0.78% with precision of 1.1%. Adulterations with sodium chloride, caustic soda, ethyl alcohol and sodium bicarbonate are detected qualitatively, even when added with water, and MilkTech indicates "SUSPECT" milk.

Keywords: milk; adulteration; quality control.

Practical Application: Detection of frauds in milk.

1 Introduction

Milk is an important food from nutritional, economic and social points of view. Milk presents more than one hundred thousand constituents, possesses many vitamins and minerals (Walstra & Jenness, 1987). In addition, dairy products are also susceptible to fraud (Hrbek et al., 2014). Moreover, authenticity is an important issue due to the concerns about the safety and quality of food (Zain et al., 2016) and has been discussed worldwide (Souza et al., 2011). The limits for the microbiological, physical and chemical parameters of milk are established by the Brazilian legislation (Brasil, 2002, 2011).

Brazil is one of the largest producers in the world and its production has grown in the last years. However, food adulteration has become more sophisticated in the recent years. Many cases have also been reported in other countries such as China, for example (Zhang & Xue, 2016). A very common problem is the adulteration of milk by adding substances such as water, sodium chloride, caustic soda, formaldehyde, and so on, that can mask or preserve milk properties as cryoscopy point, acidity, pH, as shown by Furtado & Vilela (1996). Milk can be adulterated either for financial gain or due to poor hygiene conditions of processing, storage, transportation, and marketing (Handford et al., 2016).

Even though there are recommended methods to evaluate the milk quality, it has been demonstrated that they fail in several situations, especially those with mixed adulterants. Studies on fast, low cost, and nondestructive detection methods for composition/adulterants is becoming essential for food safety

and public health (Brandão et al., 2017). In view of this, the milk chain needs new and more efficient processes to ensure the quality and safety of milk (Das et al., 2011).

The official methodology for detecting water addition is cryoscopy, which measures the freezing point of milk. However, this method is reliable only for the detection of water addition, as demonstrated by Nascimento et al. (2013). Other frauds as simultaneous addition of water and sodium chloride (or sucrose or sodium bicarbonate) can mask the cryoscopy index.

In view of these problems, the present work shows the development of a new apparatus, named MilkTech (Patent deposit number PI0805121-6, Brazil), as shown in Figure 1 (MilkTech, 2011).

It is low-cost and portable equipment for milk quality analysis, focused in the detection of the following adulterants: water, sodium chloride, sodium bicarbonate and caustic soda. MilkTech also reports the cryoscopy in an indirect way, from the determined percentage of added water. Small dairy processors would benefit from the equipment since they could use it during the collect of milk and guarantee the quality of milk in a very fast way. Moreover, dairy industries could use it in the milk pick-up truck. So, it may discard the milk before it contaminates the milk already stored.

Milktech proposes a new analytical approach to detect milk adulteration especially with water, based on electrical properties

of milk. From the electrical point of view, milk can be understood as an electrolytic solution in which the charge carriers originate from the dissociation of salts. Therefore, the electrical conductance of milk is mainly attributed to the presence of ions, in particular Na +, K + and Cl- (Walstra & Jenness, 1987). Some studies relate electrical measurements to quality control and detection of milk fraud, as demonstrated by Mabrook and Petty (Mabrook & Petty, 2002). Nascimento *et al* correlated the electrical behavior of milk with the presence of fraudulent substances. Models were proposed to fit the behavior of electrical conductivity with the added substances and statistical tools were used to validate the models (Nascimento et al., 2013).

MilkTech is based on these models. The equipment is portable, allowing the use in the field, during the milk collection. It operates from two microprocessors, one for the generation and processing of the signals, as well as calculations while the other is for control and management of the involved functions. Data is archived and analyzed, and the equipment furnishes complete reports.

In this paper we will present results obtained from this equipment in comparison with Cryoscopy and chloride test. The experiments were carried out in the laboratory and farms in Governador Valadares, Brazil.

2 Materials and methods

The experiments were performed with raw milk collected from Embrapa Dairy Cattle (in Coronel Pacheco, Minas Gerais, Brazil) with the following physic-chemical parameters: Acidity 14-18 °Dornic, density between 1.028 g.mL^{-1} and 1.032 g.mL^{-1} and cryoscopy index -0.530 °H, all in accordance with the Brazilian legislation.

Raw milk was adulterated at pre-defined concentrations with tap water, sodium chloride, sodium bicarbonate, sodium hydroxide and alcohol purchased from the trade. Parametric Tests (after verification of the assumptions) were applied from

Figure 1. Milktech apparatus. It contains an electrode and a temperature sensor, so measurements are temperature compensated. The display shows the following information: Added water in % (if any) and cryoscopy. When some reconstituting is detected, the display exhibits the message: "SUSPECT", milk added with reconstituting or high acidity.

the results generated. Field analyzes using the equipment were also performed in Governador Valadares to evaluate the behavior of MilkTech and the methodology based on Electrical measurements in a real environment. Periodic analyzes were performed in identified samples from each producer. Analyzes were performed simultaneously with the cryoscopy method. In samples that showed a reconstitution or high acidity by MilkTech were performed Dornic acidity tests and chloride detection.

3 Results and discussion

In previous studies, a statistical evaluation and validation of the descriptive/predictive model used by MilkTech was performed (Nascimento et al., 2013). After the regression using the least squares method based on the experiment, the model did not show a lack of fit in the linear model adjusted with 95% confidence and normality (Kolmogorov-Smirnov), Homoscedasticity (Levene), autocorrelation (Durbin-Watson), with 95% confidence. The P-values found were, respectively, 0.200, 0.516 and 2.009, that demonstrated the model is appropriate.

In this work, to verify the efficiency and robustness of the model used by MilkTech, a comparative study was performed. Several adulterants were used: water, caustic soda, salt, alcohol and sodium bicarbonate.

First, we show the results obtained with water addition, as presented in Table 1. Samples (raw milk) were prepared with seven different levels of water addition, up to 26% and tested with Milktech.

According to Table 1, the results obtained with MilkTech were consistent with the actual dilution levels of water. The assumption of normality was tested. It was not observed deviation from normality, with 95% confidence, by the application of the Shapiro-Wilk test, since the p-value was equal to 0.29. The T-test was also performed and there was no significant difference for the total set of samples with 96% confidence. The p-value was 0.041. The detection limit of the equipment was 0.78% of water with an accuracy of 1.1%.

MilkTech was also tested with raw milk adulterated with sodium chloride and sodium bicarbonate. Similarly to the experiments with added water, different levels of sodium chloride and sodium bicarbonate were used, and a linear calibration for each adulterant was established. The results showed that the equipment detects these adulterants, with detection limits of 0.09 g/L for sodium chloride and 0.27 g/L for sodium bicarbonate. It is important to note that Milktech does not discriminate between sodium chloride and sodium bicarbonate, but it detects both as "reconstituents" (see Table 2).

Raw milk with sodium hydroxide and ethyl alcohol were also prepared, with concentrations as shown in Table 2.

The results showed that the equipment is sensitive to small addition of NaOH, NaCl and ethyl alcohol, and quantifies water addition (in %).

In dairy farms, Milktech also showed effective performance. Analyzes were carried out in a cooperative and a dairy industry

Table 1. Milktech tests in 7 samples adulterated with water (in %), from 0 to 26%. Second column shows the actual % of added water, while the third one exhibits the result obtained with Milktech.

Sample	Water Addition (%)	Water addition detected by MilkTech (%)
1	0	0.1
2	14	13.3
3	3	2.5
4	7	6.2
5	11	10.9
6	20	19.6
7	26	26.0

Table 2. MilkTech performance compared with Cryoscopy in raw milk samples adulterated with water, sodium chloride, sodium hydroxide (caustic soda) and ethyl alcohol.

Sample	Adulteration	Quantity	CRYOSCOPY (MilkTech) (°H)	MILKTECH
0	-	0%	-0.540	OK
1	Water	3 mL/L	-0.539	0.2%
2	Water	10 mL/L	-0.536	0.8%
3	NaCl	0.1 g/L	-0.575	Reconstituting addition or high acidity
4	NaOH (P.A.) (P.M.:40,00)	0.1 g/L	-0.574	Reconstituting addition or high acidity
5	Ethyl Alcohol (98.5 GL)	0.8 mL/L	-0.539	Suspect 0.2%
	Ethyl Alcohol (98.5 GL)	4 mL/L	-0.534	Suspect 1.3%

Table 3. Comparison of cryoscopy values by the official method and MilkTech in a cooperative of Governador Valadares MG.

Sample	CRYOSCOPY (°H) (CRIOSCOPY)	CRYOSCOPY (°H) (MilkTech)	CONCLUSION (MilkTech)	CHLORIDE TEST
1	-0.539	-0.546	REGULAR	
2	-0.537	-0.542	REGULAR	
3	-0.537	-0.542	REGULAR	
4	-0.535	-0.542	REGULAR	
5	-0.538	-0.545	REGULAR	
6	-0.535	-0.540	OK	
7	-0.538	-0.540	OK	
8	-0.546	-0.540	OK	
9	-0.538	-0.542	REGULAR	
10	-0.526	-	SUSPECT	POSITIVE
11	-0.538	-0.548	REGULAR	
12	-0.541	-	SUSPECT	POSITIVE

in Governador Valadares, shown in Tables 3 and 4, respectively. Although the physical property used by Milktech is not a freezing point, there was a good correlation of the cryoscopy results.

Table 4. Comparison of cryoscopy values by the official method and MilkTech in a dairy industry of Governador Valadares, Brazil.

SAMPLE	CRYOSCOPY (°H) (Cryoscopy)	CRYOSCOPY (°H) (MilkTech)	SITUATION
1	-0.542	-0.540	OK
2	-0.540	-0.540	OK
3	-0.523	-0.540	OK
4	-0.538	-0.539	REGULAR
5	-0.458	-	16.4%
6	-0.523	-	3.4%
7	-0.540	-0.540	OK
8	-0.542	-0.540	OK
9	-0.540	-0.540	OK
10	-0.544	-0.540	OK
11	-0.548	-0.543	REGULAR
12	-0.542	-0.540	OK
13	-0.542	-0.540	OK
14	-0.542	-0.542	REGULAR
15	-0.542	-0.540	REGULAR
16	0.542	-0.544	REGULAR
17	-0.542	-0.542	REGULAR
18	-0.542	-0.540	OK
19	-0.542	-0.540	OK
20	-0.542	-0.540	OK
21	-0.542	-0.479	SUSPECT
22	-0.542	-0.540	OK
23	-0.540	-0.540	OK
24	-0.362	-0.386	40.44%
25	-0.537	-0.540	OK
26	-0.537	-0.540	OK
27	-0.537	-0.540	OK

Milktech gives cryoscopy index in an indirect way, through the determination of the water addition. It is important to emphasize the samples were Milktech indicated adulteration. In these cases the samples were considered SUSPECT by Milktech, although they were not detected by the cryoscopy. For instance, Samples 10 and 12 were submitted to chlorides test and the results attested the presence of sodium chloride confirming the suspicion of Milktech. This is a typical mixed fraud involving water and sodium chloride, which preserves the cryoscopy index, but alters the electrical properties of milk. For future experiments our proposal will be to carry out complementary tests.

4 Conclusions

Milktech presented satisfactory results for detection of the tested adulterants. The linear models used for each adulterant exhibited no lack of adjustment for a range of confidence of 96%. MilkTech's detection limits for water, sodium chloride and sodium bicarbonate were 0.78%, 0.09 g/L and 0.27 g/L, respectively. In comparison with the actual values, no significant differences were observed for a confidence interval of 95%. Therefore, the advantages of the technique based on electrical measurements are numerous: low cost, portability and fast analysis. Milktech can be used in quality control and fraud detection, simultaneously with reference methods. Even though Milktech cannot discriminate

all adulterants, it can quantify water addition. On the other hand, it is able to detect qualitatively caustic soda, sodium bicarbonate, sodium chloride and ethyl alcohol.

Acknowledgements

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