FT-IR TECHNIQUE FOR IDENTIFICATION OF ADULTERATION IN MILK

[*]Zohaib Ashraf[1], Hassan Javed Naqvi[1], Atif khan[2], Sobia Noureen[3]

[1]Department of Chemical Engineering, University of Engineering and Technology Lahore, Pakistan

[2]Department of Chemical Engineering, Dr. A. Q. Khan Institute of Technology, Mianwali

[3]Department of Bio-Chemistry and Biotechnology, University of University of Veterinary and Animal Sciences, Lahore

[1]stardawoodian@gmail.com*, [1]javednaqvi@uet.edu.pk, [2]atif12686@gmail.com

ABSTRACT: *The study was conducted due to the present situation of adulterated milk supply to the industries and to the local market in Pakistan. Milk is adulterated using different ingredients to decrease the market supply and demand gap. A rapid detection instrumentation technique such as Fourier Transform Infrared spectroscopy (FT-IR) is a rapid quality monitoring method. Five different types of milk samples are investigated including pure raw milk, artificial milk and adulterated milk samples. The FT-IR spectra showed good and effective results of adulteration detection.*

Key words: FT-IR, Milk, Adulteration, Branded Milks

INTRODUCTION

Milk is the most essential, best and easy accessible source of nutrition and an energy supplement in our daily diet. Milk provides all nutrients (i.e. fats, vitamins, carbohydrates, sugar etc.) required for human growth and good health. That is why it is readily accepted by all age groups throughout the world. To most persons pure milk is slightly sweet but milk has no pronounced taste at all. Freshly drawn milk has some specific characteristic, but not pronounced, its odor is highly volatile because when milk is exposed to air it disappears practically. Pakistan is a well-known agricultural country and the single most commodity holder of milk within the livestock sector. It comes to the third position with annual 51.6 Million Tons of milk production (Economic Survey of Pakistan 2013-2014). Cow milk contains average 4.5 % fat, 3.8 % protein, 8.5% solids not fat and ash 0.72% [1]. Milk produced whole of the year with an average consumption of 270 gram per person. Milk production reduced in the summer season especially in July and August due to high temperatures and shortage of fodder in Pakistan. Consumption of milk and milk products also increases in this season. For reducing this demand and supply gap, milk is often adulterated with different ingredients that are often danger to health. Milk is not only adulterated to reduce this gap but also to increase the money benefit by the removal of most valuable constituent of milk i.e. fat [2]. Milk is sold at very distant places from its collection. So During transportation there may be a chance of spoilage of milk. To protect milk from spoilage different preservative such as strep-to-penicillin, formaldehyde, hydrogen peroxide, sodium bi-Carbonate. Caustic soda and some time detergents are also used to maintain the pH and quality parameters of milk [3]. At the industrial level milk supplied made artificially. Artificial milk is prepared by using a very little quantity of raw milk by removing butter fat or bad quality skim milk powder. To maintain its composition, starch, flour, urea, cane sugar, vegetable oil, etc., are added as adulterants [4]. Public consume this liquid milk which has been adulterated and diluted to such an extent that there is very little nutritive value left in it, which results in malnutrition to a great extent, and different diseases are originated especially in infants at massive scale [5]. This adulteration of milk is not only limited to the farmer or milk supplier. There are some industries which are using the activity to adulterate the raw milk by adding low cost cooking oil or vegetable fat instead valuable butter fat by removing it and by increasing the quantity of milk. Unfortunately milk adulteration is not only the problem of Pakistan some other countries are also affected from this illegal and fatal activity [6]. In developed countries strict action is taken against those personals which commit such kind of act but unfortunately in some third world countries like Pakistan no action is taken such criminal personals, although punishment for such criminal acts are present in the constitution of Pakistan [7]. Keeping in view the above mentioned points, main motive for this research is to analyze the raw milk and industrially processed milk. Although in recent researches some techniques are used to determine the adulteration but these techniques are not enough to detect both major and minor adulterations therefore another advanced method is developed for rapid detection of almost all adulterants present in milk (both raw and industrial milk) [8]. This method is developed by using advance instrumentation technique known as Fourier Transform Infrared Spectroscopy (FT-IR) [9].

MATERIAL AND METHODS

Sample preparation

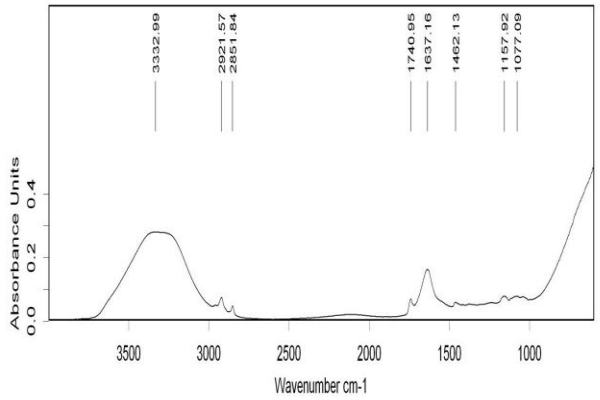
Cow milk is used for studying the components which adulterate fresh milk. Four samples are made for generating data of pure and adulterated cow milk. Adulterated samples include cow milk with urea, cow milk with sugar and combination of cow milk, sugar and urea. These adulterated samples are compared with milk samples of famous dairy industries of Pakistan. Samples were divided in three portions, one for Fourier transform infrared spectroscopy (FT-IR) analysis, second sample for adulteration and third to preserve for two days. After two days pH of the milk is declined from 6.93 to 6.60 at 20^{o}C. Sample of cow milk was diluted with water and then adulterated to reach the solid not fat (SNF) as per standard of raw milk. Sample adulterated with the sugar up to 2.4% and by urea up to 0.7%. By the addition of sugar the total solids of the milk sample increases up to 7.3%. Sample was taken for the FT-IR analysis. By the addition of urea total solids increases up to 6% and a sample was taken for FT-IR analysis and for analytical analysis to determine the total solids. The final pH of the adulterated sample reaches up to 7.02 from 6.84. After preserving raw milk sample for two days at a temperature less than 4^{o}C, sample was taken for analysis and its pH reduced from 6.83 to 6.53. This sample diluted with water and the caustic soda was added in it to increase the pH of the milk sample and then a sample was taken for the FT-IR analysis.

Analysis Technique

Fourier transform infrared Spectroscopy is the most advanced and effective technique used for analysis of samples. Infrared spectroscopy provides the rich array of different absorption bands. These bands help in providing lot of structural information about a molecule of a relevant sample [10]. It helps in providing the methodology of studying different type of materials in three states i.e. solid, liquid and gas. These qualitative aspects of FT-IR spectroscopy are one of the most powerful attributes of this versatile and diversified analytical technique.

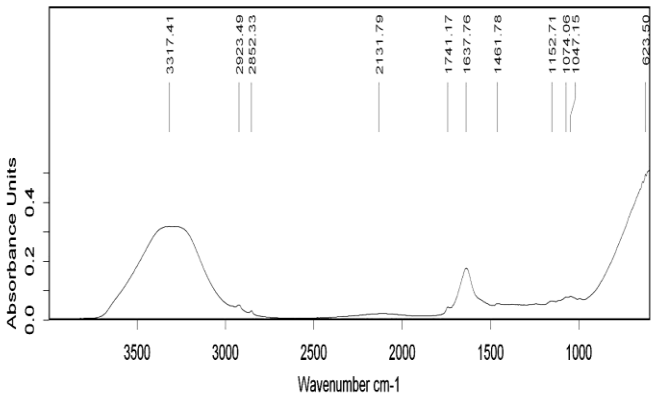
RESULTS AND DISCUSSIONS

By the comparison of pure cow milk with adulterated samples through FT-IR analysis a large difference between the spectrums can easily be observed.



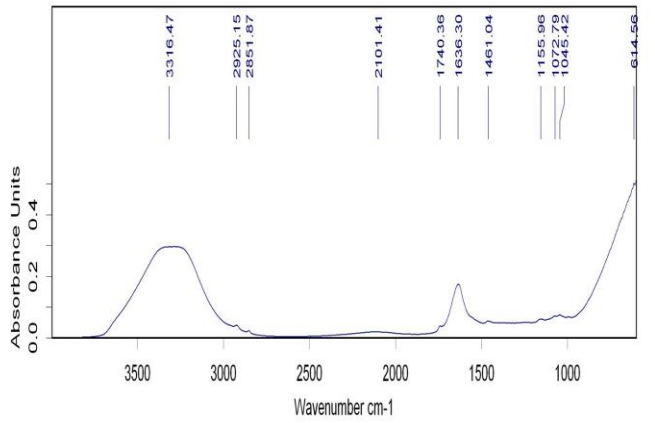
Wavenumber	Abs. intensity	Rel. intensity	Width	Found if threshold <	Shoulder
3332.9907	0.281	0.276	415.5213	57.336296	0
2921.5648	0.075	0.034	24.5671	5.856033	0
2851.8383	0.048	0.021	13.4423	3.865251	0
1740.9537	0.070	0.022	14.9204	4.338486	0
1637.1557	0.163	0.123	75.3203	24.470346	0
1462.1277	0.060	0.013	30.1316	1.907354	0
1157.9176	0.079	0.015	36.9661	2.789214	0
1077.0942	0.078	0.012	93.0417	2.321210	0

Figure 1 (Pure cow milk sample)



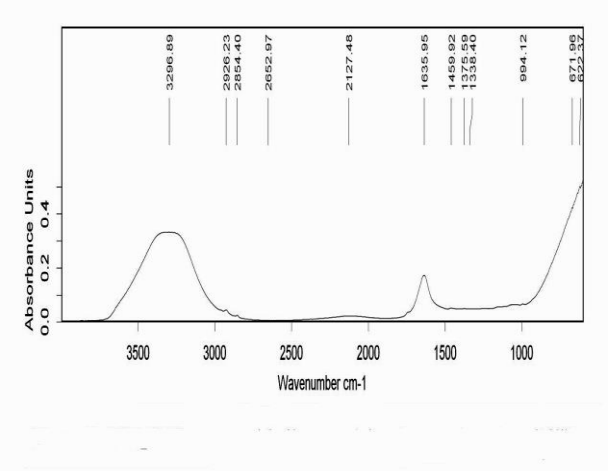
Wavenumber	Abs. intensity	Rel. intensity	Width	Found if threshold <	Shoulder
3317.4073	0.318	0.314	407.9058	60.703762	0
1637.7610	0.176	0.133	73.7227	24.627571	0
2923.4854	0.052	0.010	19.5775	26.153360	0
1741.1744	0.044	0.004	9.0336	2.969680	0
1152.7095	0.065	0.003	28.4374	16.133347	0
1047.1494	0.081	0.015	66.3986	72.244095	0
1074.0640	0.078	0.002	7.7290	6.890324	0
623.5020	0.496	0.007	3.6522	4.656263	0
1461.7780	0.056	0.001	10.8109	3.656754	0
2852.3330	0.032	0.007	11.4701	14.768781	0
2131.7877	0.022	0.000	7.6778	7.871407	0

Figure 2 (Cow milk sample with sugar)



Wavenumber	Abs. intensity	Rel. intensity	Width	Found if threshold <	Shoulder
3316.4742	0.297	0.294	407.7620	56.108673	0
1636.2950	0.175	0.132	74.8981	24.252220	0
2925.1454	0.042	0.006	19.0617	14.813497	0
2851.8742	0.024	0.005	11.7901	17.109505	0
2101.4113	0.020	0.011	261.8227	287.548004	0
1740.3558	0.040	0.002	7.2676	1.966459	0
1461.0444	0.056	0.007	30.8551	63.003407	0
1155.9546	0.062	0.004	28.2947	24.833099	0
1072.7865	0.072	0.001	11.3933	4.238621	0
1045.4164	0.077	0.012	55.1586	63.722233	0
614.5625	0.503	0.007	4.5750	4.698866	0

Figure 3 (Cow milk sample with sugar and urea)



Wavenumber	Abs. intensity	Rel. intensity	Width	Found if threshold <	Shoulder
3296.8922	0.333	0.329	403.7707	61.973492	0
1635.9544	0.174	0.131	75.2460	23.750601	0
2926.2288	0.045	0.007	16.8899	14.584106	0
2854.4010	0.025	0.004	11.1357	9.557988	0
2652.9702	0.006	0.000	6.9128	16.849819	0
1459.9207	0.052	0.004	28.1427	49.393253	0
1375.5857	0.050	0.002	16.5320	98.370193	0
1338.4041	0.049	0.001	8.2786	55.971649	0
994.1170	0.067	0.003	11.7370	9.127057	0
622.3654	0.501	0.006	4.2443	4.198180	0
2127.4804	0.022	0.001	63.4389	11.248004	0
671.9632	0.424	0.004	3.2445	1.546610	0

Figure 4 ('N' Branded Milk tetra-Pak Sample)

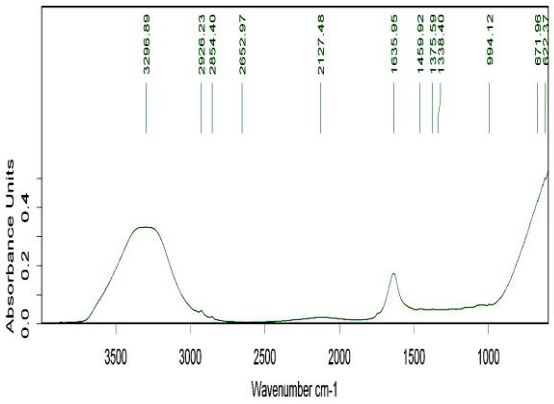


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Figure 5 ('H' Branded Tetra-Pak Milk Sample)

CONCLUSION

Figure 1 shows the spectrum of pure cow milk sample. These absorption bands are obtained with different wavelengths and different level of percentages of their absorbance. The number of peaks developed at different points within the spectrum shows different types of functional groups and hence a lot of information of molecules present within the pure cow milk sample is obtained. The specific position of peak gives the relevant attachment of functional group. From the table of FT-IR peaks relative functional groups of different wave numbers can be obtained. In figure 1 as we go from left to right, aliphatic amines, alcoholic groups, alkyl halides and different aromatic functional groups are obtained. These functional groups show the entire composition of milk, the bonding behavior of these functional groups and the absorbing intensity of these functional groups. Figure 2 shows the spectrum behavior when sugar is added in cow milk sample. If we compare this adulterated sample with pure cow milk sample the spectrum behavior obtained in this adulterated sample is almost the same but wave numbers are somewhat different. There is a slight variation in the absorbing and relative intensities of wavenumbers. These intensity differences show that the same functional groups show different bond energies and adsorption capacity if composition of milk is altered. The purpose of formation of this adulterated sample is to make sure that anything which is added in the milk should easily be detected through FT-IR. Figure 3 shows the adulterated sample of cow milk with both sugar and urea. If these results are carefully observed then large variation in peak intensities and sharpness of peak is altered at many places. Figure 4 shows the branded milk sample in Tetra-Pak packing (N). If this sample is compared with adulterated sample of Figure 3, then lot of similarities are observed specially in peak intensities and wavenumbers. Branded milk sample of another branded milk in tetra-Pak packing (H) available in the local market in Figure 5, also shows the same peak spectrum and peak behavior as in Figure 3

From this study it is concluded that the branded milk sample shows the same peak behavior and absorption band wha the adulterated cow milk sample showed. Hence this is concluded that the FT-IR spectroscopy is a simple, and rapid technique for adulteration detection of cow milk. In food industry FT-IR spectroscopy has excellent potential to use which can be replaced less efficient and more time-consuming analytical techniques for the detection of milk adulteration. It is also concluded that the Most of the branded milk being supplied into the local market are adulterated.

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