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Abstract

Introduction: Differential scanning calorimetry (DSC) greatly affected material science by empowering the estimation of a great number of physical and chemical properties. These techniques have permitted clarification of endothermic and exothermic processes at temperatures going from low (-120°C) to high (DSC 600°C and DTA 1800°C).

Aim: To differentiate between spray dried and freeze dried cow and camel milk powder using DSC technique.

Method: Both cow milk and camel milk were processed into spray dried and freeze dried powder. DSC was used differentiate between the types of drying: spray drying and freeze drying and to compare between the chemical components of the samples using enthalpy change (Δ H) measurements.

Results: The results show that show that there was a clear difference in peak 1 (fat), peak (2 and 3) (protein), and peak 4 (lactose), that means that there were really clear differences between freeze-dried Camel's milk (FDC) and freeze-dried cow's milk (FDW) cow's milk powder. Obvious changes in enthalpy of the contents of protein, fat and lactose of the various samples iindicates that the type of drying affected the composition of milk powder.

Conclusion: DSC could be could be effectively used to differentiate between the freeze-dried camel's milk (FDC) and freeze-dried cow's milk (FDW) cow's milk powder with respect to their chemical components. In addition, the type of drying affected the composition of milk especially the cow's milk.

Keywords: Enthalpy; Milk Powder; Temperature; Protein; Fat; Lactose

Abbreviations

DSC: Differential Scanning Calorimetry; SDC: Spray-Dried Camel's Milk; SDW: Spray-Dried Cow's Milk FDC: Freeze-Dried Camel's Milk; FDW: Freeze-Dried Cow's Milk

Introduction

Air-drying is an old procedure used to preserve foods in which the material to be dried is exposed to a continuously streaming hot stream of air where moisture evaporates. The phenomenon underlying this process is a complex issue involving concurrent mass and energy transport in a hygroscopic, contracting framework. Air-drying offers dehydrated products with their shelf life being extended by a year, but the quality of a conventionally-dried product is usually radically diminished compared to that of the original foodstuff [1,2].

Spray drying is the most utilized commercial technique for milk dehydration, in light of the fact that the very short time of heat contact and the high rate of evaporation that give a high quality product with a relatively low cost. presently the standard in the milk powder in-

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dustry, as the process is more efficient in terms of energy and scale (Sulieman, [3,4]). Spray drying can be used to produce stable powders with new possibilities for industrial applications. This technique has been widely used in the food and pharmaceutical industries [5].

Freeze-drying has been utilized to produce for a long time and depends on sublimation, occurring in three stages; pre-freezing, primary, and secondary drying [5]. Freeze-drying turned into a standard processing technique in the bio-industry sector, where it empowers stable products of high quality to be produced. In the drying process, the solvent as well as the suspension medium is solidified at a low temperature and thereafter sublimated from the solid state directly into the vapor phase. Freeze-drying has turned out to be standout amongst the most critical processes for the preservation of heat-sensitive biological material [6-8].

Differential Scanning Calorimetry (DSC) is a highly sensitive technique to study the thermotropic properties of many different biological macromolecules and extracts (Chui and Prenner, 2011). In this technique the difference in the amount of heat required to increase the temperature of a sample and a reference are measured as a function of temperature. Both the sample and the reference are kept up at about a similar temperature all through the test. Generally, the temperature program for a DSC investigation is planned to such an extent that the sample holder temperature increases linearly as a function of time. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned [9].

The main application of DSC is in studying phase transitions, such as melting, transitions, or exothermic decompositions. These transitions involve energy changes or heat capacity changes that can be detected by DSC with great sensitivity. The objective of the present study was to differentiate between spray drying and freeze drying camel and cow milk powders using Differential Scanning Calorimeter Measurements (DSC) System.

Materials and Methods

Materials

Fresh cow and camel milk samples were supplied by Al Ain Dairy Company during the year (2008). In addition, commercial cow milk powder samples were bought from a local supermarket in Alain, United Arab Emirates to be used in the study.

Spray drying of milk

Production of camel milk powder was completed in two stages evaporation and spray drying, as follows:

Camel milk was concentrated to 20% - 30% total solid using rotary evaporator (Rotavapor R II, Buchi, Switzerland) at 80°C. The camel milk concentrate was dried using a spray dryer (FT 80 Tall from Spray Dryer, Arm field Ltd., UK). Different drying conditions were employed. Air inlet temperature was set at (200°C - 220°C), air outlet temperature was between (98°C - 105°C), pump speed was set at (3 - 5) arbitrary units and the outlet air relative humidity ranged between (1.2 - 5.8) percent.

Freeze-drying of milk

Hundred ml raw camel's milk and cow's milk were placed in especially glass bottles for freeze-drying, then glass containers was placed in a deep freezer operated a temperature of -75°C for 24 hours, then the glass bottles placed in a freeze-dryer, under the temperature of (-50°C to -75°C), under vacuum, to obtain the Freeze-dried powder.

Differential scanning calorimeter measurements (DSC)

An SDC Q100 differential scanning calorimeter (AT Instruments Inc., New Castle, DE) equipment with nitrogen refrigeration cooling system (RCS) and hermetic pans were used. DSC was conducted on camel's milk and cow milk powder; 5 mg of each sample was pipetted into the aluminum pan and hermetically sealed. The temperature was raised from 20°C to 250°C at rate of 5°C/min. DSC was used to compare the results as the follows:

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Enthalpy ΔH

The heat content of a chemical system is called the enthalpy (H). The enthalpy change ΔH is the amount of heat released or absorbed when a chemical reaction occurs at constant pressure. The enthalpy change was calculated according to the following formula: $\Delta H = H$ final – H initial

Where:

 ΔH is the enthalpy change.

H final is the final enthalpy of the system, measured in joules. In a chemical reaction, H final is the enthalpy of the products. H initial is the initial enthalpy of the system, measured in joules. In a chemical reaction, H initial is the enthalpy of the reactants.

Type of drying

The DSC was used to differentiate between the types of drying: spray drying and freeze drying and to compare between the components of the samples. In this method, the samples were placed in DSC; the amount of each was 5 mg. Two samples from spray dried milk powder (camel's milk and cow's milk), and two samples from freeze dried milk powder (camel's milk and cow's milk) were used.

Type of milk

The DSC was used to differentiate between the types of milk used in the study: camel milk and cows' milk. Two samples from cow's milk (spray dried and freeze dried) powder were placed in DSC, the amount of each 5 mg, the first powder produced by freeze-dried, and the second powder produced by spray-drying to compare the effect of type of drying to the component.

For camel milk, two samples from camel's milk powder (spray dried and freeze dried): were placed in DSC, the amount of each was 5 mg, This experiment was conducted to determine the effect of type of drying on the different components on camel's milk powder.

Effect of temperature

The effect of temperature on the different samples was determined. Three samples of spray-dried of each milk powder were placed in DSC, the amount of each was 5 mg, the temperature used in drying of the first sample, and second sample and third sample were 200°C, 210°C and 220°C, respectively.

Results and Discussion

It is known that processing may in part or absolutely influence the quality of a food product. Different changes may happen in physical, chemical as well as biological characteristics of foodstuffs during processing, storage and distribution. The criterion of quality to expanding significance to consumers' decision. In this way, industrial products and ingredients are relied upon offer different advantageous properties (taste, health promotion, safety, etc.) that compare to those of new products. In the meantime, new market requests are rising that could concern freeze-dried products.

Differential scanning calorimetry measurements (DSC)

The scanning methods were carried out in order to study the effects of spray and freeze drying on different components of cow's and camel's milk, and also the effect of temperature on the different components of spray dried and freeze dried powder.

The data in table 1 show that there was a difference in peak 1 (fat), peak (2 and 3) (protein), and peak 4 (lactose), that means that there were really clear differences between freeze-dried Camel's milk (FDC) and freeze-dried cow's milk (FDW) cow's milk powder.

The data in table 2 show the difference between spray-dried cow's milk powder and spray-dried camel's milk powder. It was found that there was a difference in enthalpy in peak 1 (fat), peak 2 and peak 3 (protein), and it was found that the type of drying affected the composition of milk especially the cow's milk.

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1	9	7	

Milk powder	Peak1	Peak2	Peak3	Peak4
FDC	8.32	32.67	1.214	11.88
DFW	3.152	56.99	4.620	8.937

Table 1: The difference between freeze-dried Camel's milk and cow's milk powder.

FDC: Freeze-Dried Camel's Milk; FDW: Freeze-Dried Cow's Milk

Milk powder	Peak1	Peak2	Peak4
SDC	1.752	39.22	6.216
SDW	0.326	30.40	11.24

Table 2: The difference between spray-dried of camel's milk and cow's milk powder.

SDC: Spray-Dried Camel's Milk; SDW: Spray-Dried Cow's Milk

The data in table 3 show that there was a difference in enthalpy at peak 2 (protein) of freeze-dried cow's milk powder which had a higher value when compared with that of the spray-dried cow's milk powder.

Milk powder	Enthalpy in peak 2	Enthalpy in peak 3
FDW	58.69	4.869
SDW	41.71	6.330

Table 3: The difference between spray-dried and freeze-dried cow's milk powder.

FDW: Freeze-Dried Cow's Milk; SDW: Spray-Dried Cow's Milk

The data in table 4 show the comparison between freeze-dried camel's milk compared with spray-dried camel's milk, the enthalpy at peak1 (fat) was higher in freeze-dried camel's milk, while enthalpy at both peak 2 and 3 (protein) was higher in spray dried camel's milk.

Milk powder	Peak1	Peak2	Peak3
SDC	4.700	38.88	5.278
FDC	8.8400	33.19	1.408

Table 4: The difference between spray-dried and freeze-dried of camel's milk powder.

SDC: Spray-Dried Camel's Milk; FDC: Freeze-Dried Camel's Milk

Effect of temperature

The data in table 5 show that the temperature affected cow's milk spray-dried powder, mainly in peak1(fat), moreover, high temperature adveresly affected fat content.

Temp.°C	Peak1
210°C	2.764
220°C	0

Table 5: Effect of tempeture on cow's milk powder.

The data in table 6 show that the temperature affected camel's milk powder at peak 1 (fat), peak 2 and 3 (protein), high temperature adversely affected the fat and protein contents.

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Temp.°C	Peak1	Peak 2
200°C	4.020	39.31
210°C	1.501	37.71
220°C	1.110	23.22

Table 6: Effect of tempeture on camel's milk powder.

Discussion

Differential Scanning Calorimetry is used to measure the specific heat capacity of thermally induced events as a function of temperature [10]. The differential heat flow from the calorimeter is temperature subordinate and is alluded to as a thermoanalytical curve. As the scan rate is consistent, the time integral of the deliberate differential heat flow provides the energy of the sample [11].

Considering the capacity to quantify enthalpy changes and phase transitions, there are different applications for such a flexible apparatus, these include: application to proteins, for pharmaceutical interest, protein mutations, protein-ligand interactions, protein folding, nucleotides, other macromolecules, lipids, drug-lipid interactions and protein-lipid interactions [12-15].

The application of DSC to proteins (e.g. enzymes), their thermodynamic properties are vital, and one of the soonest DSC applications was to think about thermally instigated, helpful conformational changes of small proteins [12,16]. However, small molecules don't yield great information unless they aggregate, showing intermolecular cooperation. The application of DSC to protein denaturations was depicted by [17] who revealed that thermal transition was synonymous with the protein segment work, recommending that the thermogram can be utilized to distinguish the states in denaturation [18]. Thus, protein thermodynamics, during unfolding, is measured as an enthalpy change, as a function of temperature.

Differential Scanning Calorimetry-based analysis of the thermal denaturation of proteins gives an understanding into the unfolding procedure and forces engaged with compliance stability. During protein denaturation there are diverse thermodynamic states, with numerous tiny states. This procedure is profoundly agreeable with disturbance of many of many forces and bonds, including hydrogen bonds, hydrophobic interactions, and many non-covalent interactions.

DSC takes into consideration the immediate investigation of thermal stability, over a very large concentration range, without light, therefore photosensitive proteins such as bovine lens crystallin's can be analyzed. Conversely protein folding can also be studied, investigating thermotropic changes in various environments.

Heat capacity with respect to thermally induced protein denaturation has revealed thermodynamic data about the distinctive states as it relies upon three major factors. The first relates to the essential structure of the protein and contributes from extending and bending to the rotating of internal bonds. The second factor is based on non-covalent interactions from the secondary and tertiary structures.

At last commitments from the hydration influence the heat capacity. The essential structure gives the most critical commitment, followed by hydration, and less impact from the noncovalent secondary and tertiary interactions.

Phospholipids are a standout amongst the most studied lipids by [19]. One of their significant points of interest is that pure synthetic phospholipids experience changes at well-defined temperatures in light of their structure. Hence, the transitions are effectively reproducible and patterns can be built up inside systematically changed lipids (e.g. progressively expanding chain length). Pure lipids are analyzed as aqueous dispersions, framed from a lipid film, by mechanical agitation, such as vortexing. They contain multilamellar vesicles (MLV), which are closed multi sheaths comprised of concentric bilayers that are separated by fluid spaces. MLVs are the predominate frame used to investigate lipids, as they give the clearest resolution of stage changes with precise enthalpy values.

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Differential scanning calorimetry of cholesterol has been applied to concepts such as the lipid-raft in cellular membranes and the presence of stage isolated liquid spaces in cholesterol-lipid blends Cholesterol is one of the key lipids in eukaryotic cells, with basic roles in metabolism, hormone production, and arrangement of several vitamins. Aside from the conceivable lipid rafts the role of cholesterol on requesting nearby lipids has been studied. Additionally blends of PC, SM, and cholesterol have been utilized to shape raft microdomains, as various concentrations of components result in various stage developments, which go about as potential targeting sites of pharmaceutical products [20,21].

Conclusion

Based on the significant findings of the present study, the Differential Scanning Calorimetry Measurements DSC could be successfully engaged in differentiation between the freeze-dried camel's milk (FDC) and freeze-dried cow's milk (FDW) cow's milk powder with respect to their chemical components (protein, fats, lactose) as clearly appeared in their different peaks. The changes in enthalpy of the contents of protein, fat and lactose of the various samples indicates that the type of drying affected the composition of milk powder More-over, there was a difference in enthalpy in peak 1 (fat), peak 2 and peak 3 (protein), therefore the type of drying affected the composition of milk especially the cow's milk.

Differential Scanning Calorimetry stays one of the essential devices for thermodynamic analysis. Advancements s with programming take into account simple elucidation of thermodynamic information, which again make DSC an extremely appealing technique. So, it is highly recommended to use DSC in comparison between various food items.

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