Analysis of diffuse reflectance spectra of powdered milk and their relationship to technological parameters

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Abstract

Introduction. In order to improve products for baby food a research of animal milk has been conducted. The study of diffuse reflectance spectra of various food products makes it possible to determine the different physical and chemical characteristics.

Materials and methods. Infrared reflection spectra of powdered milk, which is recommended to be used in infant formulas, were tested using the device "Infrapid-61". Diffuse reflectance spectra of powdered milk products were studied within 1330-2370 ran in increments of 10 nm.

Results and discussion. The diffuse reflectance spectra of powdered milk of such domestic animals like goats, sheep and mares are quite similar, but at certain wavelengths there are significant differences. All the tested reflection spectra of mare and goat milk are similar in form. The reflection spectrum of sheep milk is slightly different from the previous ones. So at a wavelength of 1720 nm for all three spectra minimum reflection is observed, but in the spectrum of mare milk this extremum is considerably lower. Similar conclusions can be drawn by analyzing the spectra at wavelengths 2310 and 2350 nm. The special features include the fact that in the range of 2010-2220 nm wavelength reflection spectrum of mare milk is a monotonic curve with one extremum at a wavelength of 2110 nm. At the same time, the reflection spectra of sheep and goat milk show two extremes at wavelengths 2060 and 2170 nm. An important spectral range is within 1480-1500 nm wavelengths, which is responsible for the presence of protein in the samples. Especially low minimum characteristic of mare milk, that has the least amount of protein in its chemical composition, was confirmed by independent experiments. The protein content for goat and sheep powdered milk does not differ significantly. This conclusion is confirmed qualitatively, based on analyzes of reflection spectra.

Conclusions. The tests of diffuse reflectance spectra in the near infrared wavelength revealed significant differences in the wavelength division for goat, sheep and mare powdered milk and made it possible to carry out a qualitative analysis.

Introduction

The basis of dairy products for baby food, produced in Ukraine, is cow's milk, the components of which make undesirable impact on immature baby's body. That is why the cow milk prototyping is an urgent problem in the production of baby food. As a substitute for cow milk the milk of domestic animals - goats, sheep and mares was suggested to examine. Currently numerous infant formula are available, they are breast milk substitutes that are considered adapted to a baby's body. Yet, children who are deprived of breastfeeding and get bottle-feeding do not get the amount of natural nutrients, which is found in human milk. To balance the composition of adapted formula different blends of vegetable oils, vitamins, mineral complexes, etc. are added. No animal milk can be compared to human milk in its composition.

Recently the number of different allergic diseases among children is inclined to increase steadily. Clinical implications of allergic reactions, mainly related to dietary habits, can be observed from infancy. Food allergies of infants are mainly allergies to cow milk protein. Its prevalence among infants up to twelve months is not known with certainty, though, it is estimated 2 to 6%. Often the diagnosis is made based on the symptoms of skin rash, seborrhea, dermatitis, functional disorders of the digestive system, nasal breathing disorders, sleep disorders.

In order to improve products for baby food the studies of milk of such animals as goats, sheep and mares have been undertaken. Along with the standard methods of determination of substances infrared spectroscopy method has recently gained widespread use. This is due to the fact that this method gives the possibility of rapid, non-destructive analysis of substances using modern computer technology. Reflection spectra of various food has been studied by scientists

from many countries for over a decade. However, the interesting features of infrared reflectance spectra of powdered milk offered to use in baby food have been revealed by us with the help of device "Infrapid-61." The study of diffuse reflectance spectra of various food products makes it possible to determine different physical and chemical properties: moisture, content of proteins, fats, sugars, starch and so on.

Materials and methods

The object of the research were samples of powdered animal milk: goat, sheep and mare milk which is going to be used to improve baby food. This milk was received in semi spray dryer "Nyro-Atomizer" with a 0.9 m# working volume of camera and producing capacity of evaporated moisture up to 10 kg / h. Dryer makes it possible to ensure the temperature of the drying agent in the range 120 ... 250 "C at the inlet of the dryer and 80 ... 100 ^{0} C at the outlet. Recently, along with the standard methods of determination of substances the method of infrared spectroscopy gained widespread use, particularly in the near infrared wavelength. Therefore, to study samples of powdered milk products the device "Infrapid-61" operating in the wavelength range 1330-2370 nm was used.

Automatic measurement of reflectivity in this wavelength was performed in increments of 10 nm, allowing us to obtain diffuse reflection spectra of different kinds of powdered milk products. Thus there was no need of special sample preparation because it had a homogeneous structure. Therefore, samples were kept under the same conditions with low humidity, directly loaded into sample compartment and analyzed within a few minutes. Another feature of this method is that it does not require special chemicals sample preparation.

The chemical composition of these products was determined by standard methods. Mass fraction of protein was determined by turbidimetric method. The method is based on measuring the luminous intensity of scattered solid or colloidal particles that are suspended in solution. The intensity of light scattering, defined by turbidimeter, informs us about the concentration of the substance.

For the experiment, 0.5 g of the product must be weighed within the accuracy to 0.001 g in a conical flask of 250 cm^3. Add 50 cm^3 burette 0.05 mol / dm ^{3} sodium hydroxide solution. Close the flask with a stopper and shake for 15 minutes in mechanical shakers. 10 minutes is necessary to centrifuge (speed 6000 min-1), followed by 5 cm^3 of centrifugate dispensed with pipette into a volumetric flask of 50 cm^3. Fill up the contents of the flask to the mark with sulfosalicylic acid. The flask is to be quickly flipped 2-3 times and the solution poured into sample compartments with a layer thickness of 5 mm. Measure for Optical density (wavelength 550 nm). Mass fraction of protein is determined by the calibration curve. Making the calibration curve - to make the calibration curve we select samples with different mass fraction of protein in the range that occur naturally (8 to 20%). Range interval in protein content of samples must be within 1%. The number of samples should not be less than 10. Accuracy of values increases with sample's number.

Mass fraction of lactose in milk was determined by iodometric method. The gist of the iodometric method of determining lactose is as follows. Known amount of copper sulfate (CuS04) in excess is added to a known quantity of milk with unknown concentration of lactose. Part of the copper is used for lactose oxidation and the other part remains unchanged in divalent state. This reaction takes place in an alkaline environment that is created by adding alkali (NaOH). We do not know yet the amount of copper that has reacted with lactose. To culculate it, the known volume of solution of iodine (12) and sodium hydroxide (NaOH) is added to the mixture. As a result we get two compounds -sodium iodide and yodad (NAI and NalO). Copper, which does not enter in reaction with lactose, reacts wi'.h sodium iodide (NAI), resulting in the formation of molecular iodine (12), which again goes into ionic state after reaction with sodium thiosulfate (Na2S203). The dose of thiosulfate solution is proportional to the dose of molecular iodine, which was formed, and to the dose of bivalent copper, which did not react with lactose. Since the initial volume of the solution of copper sulfate and its concentration is known, the calculations set amount of copper, which came in reaction of lactose oxidation, and then the content of the lactose in milk.

For the experiment, 25 g of milk must be weighed within the rccuracy to 0.01 g in a volumetric flask of 500 cm^3. Add distilled water to half the volume of the flask. Then add 10 cm3 of solution CuS04 (Fehling reagent I) with a pipette. Add 4 cm^3 of 1 mol / dm^3 sodir n hydroxide (NaOH) with pipette. Stir the mixture and fill up the substance of the flaik to the mark with

distilled water. Stir and leave still for 30 minutes. The liquid is filtered through a filter paper (the first 10 ... 20 cm^3 of filtrate is extracted;. Proceed to filter into a dry flask. 50 cm^3 of the filtrate is measurde with a pipette and put into a conical flask of 250 cm^3. Add 25 cm^3 of 0.1 mol / dm^3 solution of iodine (12) with a pipette. Slowly add 37.5 cm3 of 0.1 mol / dm^3 sodium hydroxide (NaOH), and constantly stir the substance of the flask. The flask' is closed with a stopper and left in the dark for 20 minutes. AdJ 8 cm^3 0.5 mol / dm^3 of; hydrochloric acid (HC1) from a cylinder, and at this moment we can observe allocatiftn of molecular iodine. Disengaged iodine is immediately titrated. b> 0.1 mol / dm^3 of sodium thiosulfate ($Na_2S_20_3$) to the appearance of straw yellow color. Add 1...2 cm^3 of l%(starch solution; at this mixture color turns dark blue due to the reaction of starch and iodine. Continue adding sodium thiosulfate until the discoloration of the mixture, which will be held using 1...2 extra drops of thiosulfate. Record total volume of sodium thiosulfate, which was used for titration, cm^3.

Next, the control experiment is held. Instead of the filtrate 50 cm^3 of distilled water is measured into a flask and the experiment is performed in the same way and with the same reagents as in the main experiment, starting with putting 50 cm^3 of the filtrate into a conical flask of 250 cm^3.

Mass fraction of lactose L (%) is calculated by the formula:

$$L = \frac{0,01801 \cdot (V_1 - V_2) \cdot 100 \cdot 0,97}{m},$$

where *0.01801* is the amount of lactose corresponding to I cm^3 of 0.1 mol / dm^3 iodine solution, g;

V) is the amount of 0.1 mol/dm^3 solution of $Na_2S_20_3$ which was spent on the titration of iodine in the control experiment, cm^3;

V is the amount of 0.1 mol/dm^3 solution of $Na_2S_20_3$ which was spent on the titration of excess iodine in the filtrate, cm^3;

0.97 is the amendment established empirically;

m is the mass of milk in 50 cm^3 of filtrate, g

Fat content in milk was determined by acid method. The method is based on milk fat separation under the action of concentrated sulfuric acid and isoamyl alcohol, followed by centrifugation and measuring the amount of fat released in the graded part of butyrometer.
10 cm^3 of sulfuric acid is poured into two milk butyrometers (1-6, 1-7) with a dispenser, and careft lly so the liquids do not mix add 10.77 cm^3 of milk with a pipette. 1 cm^3 of isoamyl alcohol is added to each butyrometer with a dispenser. Butyrometers are closed with dry plugs. Butyrometers are shaken until proteins get dissolved, turning them at least 5 times, so that the liquids are completely mixed up inside. Butyrometers are set on a boiling-water bath for 5 minutes at 65 ± 2 °C. Taken off the bath, butyrometers are put in centrifuge cups with their graduated parts down. Butyrometers are placed symmetrically opposite each other. They are centrifuged for 5 min. Each butyrometer is removed out of the centrifuge,
jid by moving rubber stoppers regulate fat rod so that to keep it in the graded part of butyrometer. Butyrometers are put on a boiling-water bath at (65 ± 2) ° C with their stoppers down for 5 minutes, when the water level in the bath should be somewhat higher than fat level in the butyrometer. Butyrometers are taken out one by one and then calculation of fat is made immediately.To analyze the reconstituted milk it undergoes heating up on a boiling-water bath at (65 ± 2) ° C for 5 min three times between each centrifugation. Butyrometer indicators show mass fraction of fat in milk.

Results and Discussion

After milk research was made we received the data given in Table I. The results obtained by infrared spectroscopy given in Figure 1 showed that the diffuse reflectance spectra of powdered milk of animals such as goats, sheep and ms-es are similar in nature, but at certain wavelengths

there are significant differences.

Table 1

Composition of powdered animal milk

Milk	Protein mass fraction, %	Fat content, %	Mass fraction of lactose, %
Sheep	25,2	32,0	21
Goat	29,6	22,0	40,0
Mare	16,1	12.0	66,0

Comparative analysis of the diffuse reflectance spectra of powdered milk samples showed that all the tested reflection spectra of mare and goat milk are similar in form. It should be emphasized that the reflection spectrum of sheep milk is slightly different from the previous ones. So at a wavelength of 1720 nm for all three spectra minimum reflection is observed, but in the spectrum of mare milk this extremum is considerably lower. Similar conclusions can be drawn by analyzing the spectra at wavelengths 2310 and 2350 nm. The special features include the fact that in the range of 2010-2220 nm wavelength reflection spectrum of mare milk is a monotonic curve with one extremum at a wavelength of 2110 nm. At the same time, the reflection spectra of sheep and goat milk show two extremes at wavelengths 2060 and 2170 nm, respectively.

An important spectral range is within 1480-1500 nm wavelengths, which is responsible for the presence of protein in the samples. Especially low minimum characteristic of mare milk, that has the least amount of protein in its chemical composition, was confirmed by independent experiments. As for the goat and sheep powdered milk, the protein content of these products does not differ significantly. This conclusion is confirmed qualitatively, based on analyzes of reflection spectra. Interesting results were obtained using electrophoresis in the study of protein fractions of the samples. It was found that proteins of goat and sheep milk contain different amounts of casein in its composition. This fact may explain some differences in reflectivity coefficients of goat and sheep milk for this range of wavelengths. In the spectral range 1930-1950 nm the coefficients of reflectivity samples are close. This range of wavelengths characterizes humidity of any food product. It should be mentioned that powdered milk was obtained for baby food production. Therefore, it imposed more stringent requirements for moisture content, which should not exceed 4% in such product. Product moisture control can be easily carried out, using quantitative analysis by NIR spectroscopy. Interestingly, the spectral distribution at a wavelength of 2110 nm mare milk reports a deep minimum, confirming the low content of casein and protein. The comparative analysis in this part of the spectrum again confirms the fact that the mare milk contains much less protein and casein (1.5-2 times) compared to sheep and goat milk. Noteworthy is the wavelength of 2350 nm, where there is minimum reflection for all three samples. This wavelength carries some information about the content of fat in the product. It should be noted that, according to previously obtained data, the fat content in sheep milk is the biggest, quantitative content of fatty acids in sheep milk is quite different from the content of some fatty acids in mare and goat milk.

Conclusions

The research of diffuse reflectance spectra in the near infrared wavelength revealed significant differences in the spectral distribution for goat, sheep and mare milk and made it possible to carry out a qualitative analysis. It was found out that these studies enable us to analyze the composition of the products, or to identify similarities and differences of the samples. Diffuse spectroscopy method provides a comparative analysis of the products, but requires significantly less time to get results than the methods determining each indicator in the products.

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