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THE CHANGES OF SOME CHEMICAL INDICES OF OF NUTRITIONAL VALUE OF STORED MILK POWDER

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The gradual decrease of the organoleptic and nutritional quality of stored milk powder is usually brought about by the condensation Maillard's reactions ("non enzymic browning") and by the autoxidation of fat. More than two decades ago, extensive research work conducted specially in the United Kingdom showed that a principal prerequisite for the inhibition of nonenzymic browning was a possibly low moisture level of milk powder. (preferably 2—3%), and that an effective checking of autoxidation could be created by a strong preheating of milk prior to its evaporation and drying. It seems worthwhile to mention that such undesirable changes of milk powder as a drop in its solubility, hardening, flavour deterioration and decrease of digestibility are, in fact, the consequences of complex reactions between the free amino-groups of proteins and the carbonylic groups of milk sugar, and also of the rehydrative changes in lactose, which reactions, on turn, are dependent upon the moisture level of milk powder.

In the last years various chemical tests for the control of milk powder quality have been perfected as f.ex. the determination of the reducing capacity, formation of sulphydril groups or of oxidation products of fatty matter. Our attention has been particularly drawn to the method elaborated by Keeney and Bassette [1] based on the determination of 5-hydrooxymethylfurfural (HMF) in the reconstituted milk after a standard hot digestion with oxalic acid. After treating the deproteinized sample with the thiobarbituric acid, and intensification of colour caused by the formed HMF was obtained by the above mentioned authors. The HMF formed after digestion with oxalic acid, according to Gottschalk [2], gives information about the amount of 1-amino-1-deoxy-2-ketoses which, as precursors of HMF, are characteristic of the earlier stages of Maillard's reactions.

The chief objective of our investigations was to ascertain to what a degree the results of Keeney and Bassette's test are convergent with some other methods of determining the deteriorative changes of stored milk powders. For this purpose, two batches of freshly manufactured spray full milk powders were used. The only difference in the manufacture of powders was that in batch I the milk was preheated to 115°C over 15—20 sec., and in batch II — only to 105°C over 15—20 sec. The powder was cooled, packed in hermetic 0.5 kg polyethylene bags and stored for 20 weeks at either 20° or 37°C. Analyses were made at intervals of 2—5 weeks, the following determinations, inter alia, being executed: (i) moisture content; (ii) solubility (by the official standarized methods; (iii) Keeney and Bassette test for HMF [1]; (iv) peroxydes in total milk powder lipids after Hills-Thiel [3], the lipid extraction done according to Greenbank and Pallansch [4]; (v) titratable acidity of lipids; (vi) total nitrogen after Kjehldahl; (vii) formol nitrogen, analogically to fluid milk; (viii) thermal denaturation of proteins according to Ntailianas and Grimbleby [5].

Additionally, in connection with the investigations by Ford and Porter [6], who have found that the determination of the binding capacity of the dye Orange G by milk proteins gives results similar to those obtained by the more complicated method of Carpenter et al. [7], for some samples we determined the binding capacity of proteins in respect to Orange G and Amide Black dyes [8].

Figures 1 and 2 present the results of the most part of our analyses in the form of curves platted against the time of storage.

From these graphs it results that the moisture content in samples was maintained within the limits of 2—3%, that is on the level which should almost preclude Maillard's reactions. Some fluctuations in the moisture content may be the result of usual differences in the composition of powder in various bags, and the more distinct increase of water content in the first week(s) was probably caused by the absorption of moisture from air in the initial period of cooling the powder in the paper bags before packing in into small polyethylene bags.

The solubility of milk powder after 20 weeks' storage at 20° decreased from the initial 99 to about 95%, while in powders kept at 37° the solubility dropped down to 93—95% at the end of the storage period. On the whole, however, in view of the existing standards, the decrease of solubility cannot be considered high.

Also the increase of perioxide indices and the acidity of total milk powder lipids proved to be rather insignificant and capable of being distinctly established more no sooner than after 16 weeks of storage both at 20 and 37°C.

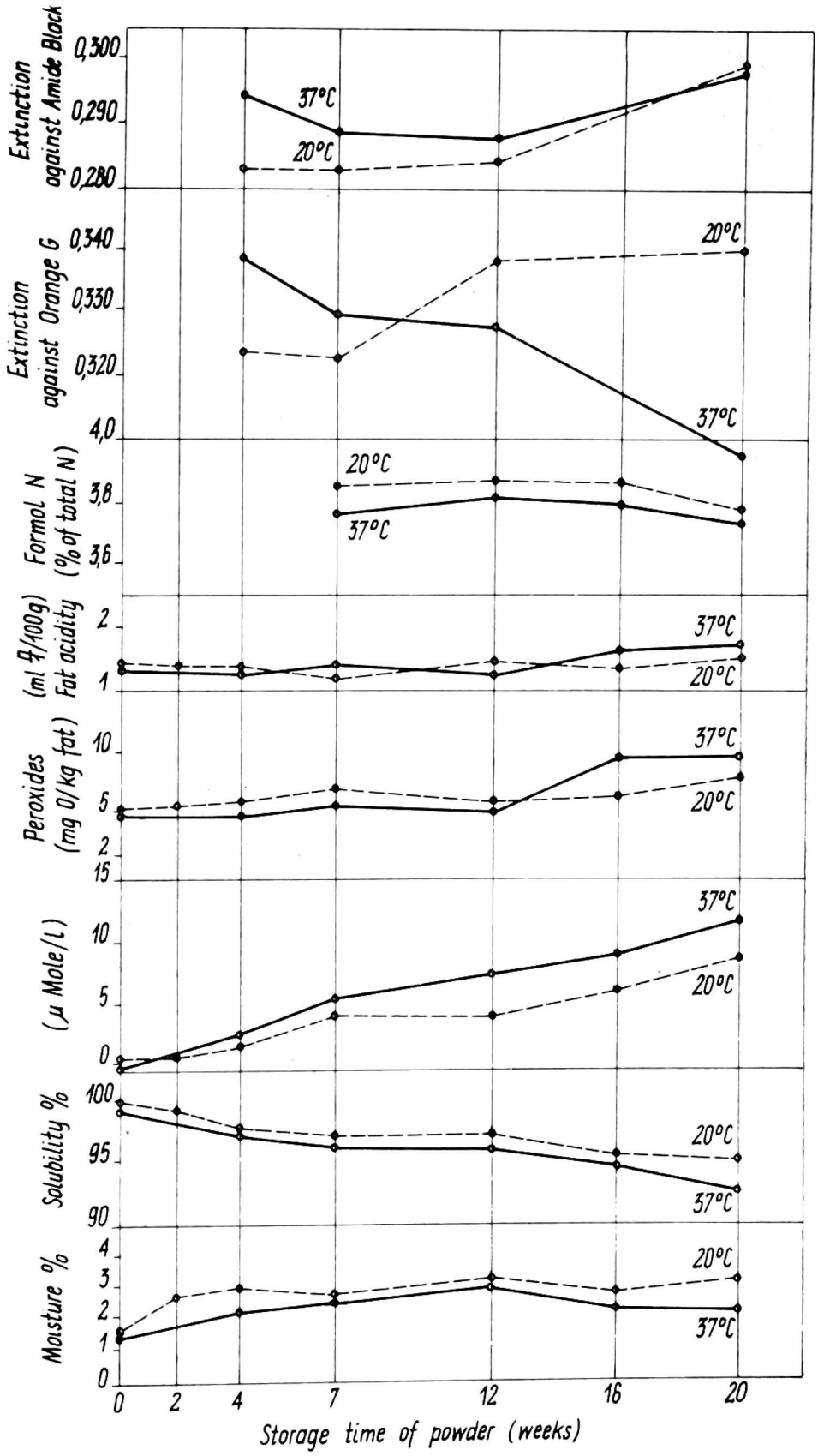

Figure 1. Changes of various chemical indices of the quality of milk powder during the 20-weeks' storage at 20 and 37°C Powder Batch No. I

The determinations of the so called formol nitrogen (expressed in pct. of total N (have kept all time practically within the limits 3.8—3.9%, and only in the last weeks there is a tendency to a slight drop to about 3.7% (more exactly to 3.75%). These results would indicate that there

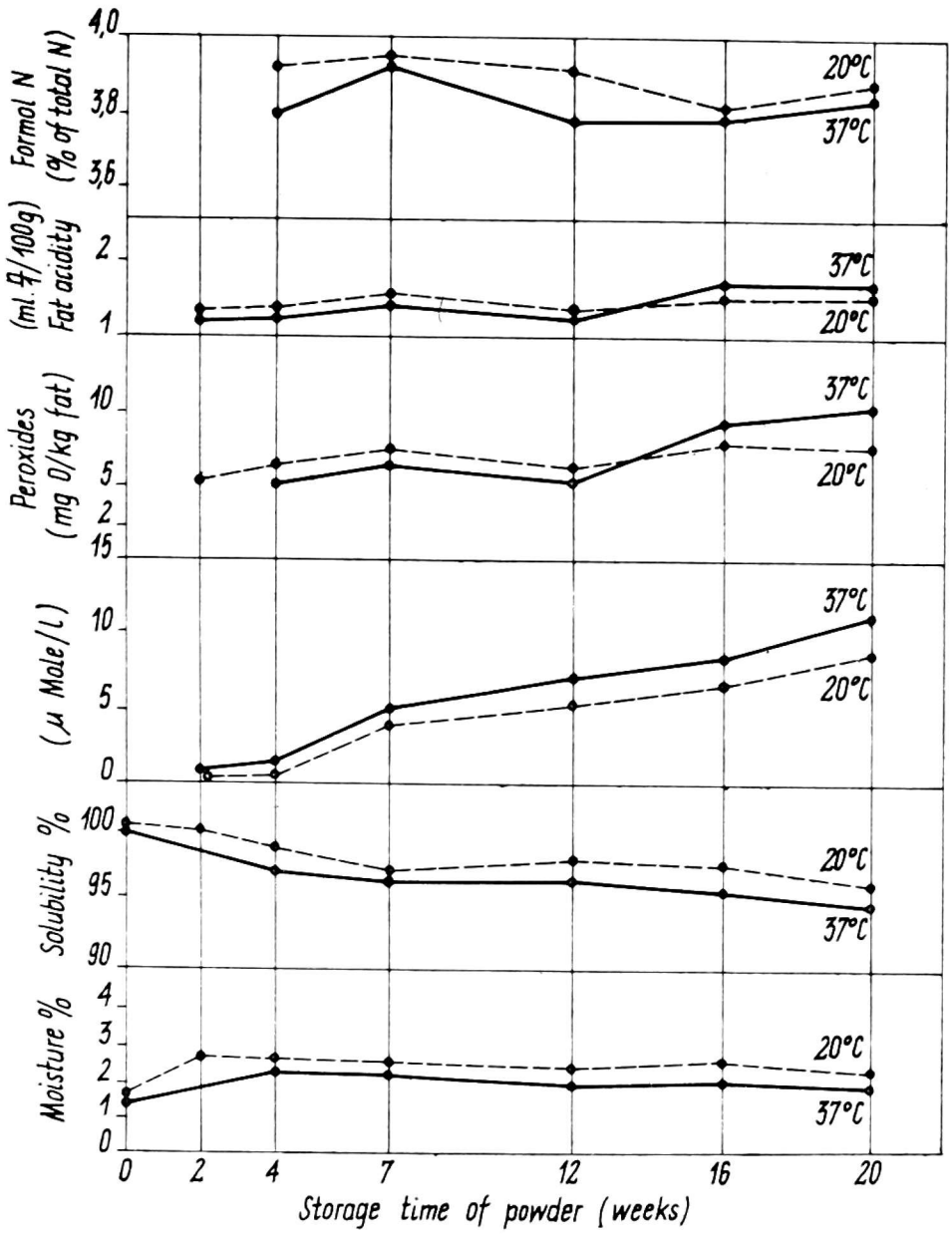

Figure 2. Changes of various chemical indices of the quality of milk powder during the 20-weeks' storage period at 20 and 37°C
Powder Batch No. II

were not any appreciable changes in the amount of free aminogroups in powders, or at least that the formol determinations are not sensible enough to detect small changes in the amount of free aminogroups of stored milk powders. In a more drastic way, this confirmed by the results of determinations of Orange G or Amide Black binding capacities, their irregular values (see Fig. 1) being probably caused by difficulties in securing an uniform impregnation of milk powder proteins with the dyes in question.

In view of the generally unsignificant, or undistinct, or irregular changes of the above mentioned chemical indices of milk powder, the results of HMF determinations are remarkable by their regular and distict changes throughout the whole storage period. The initial amount

being lover than 1 μM of HMF per 1 litre of reconstituted milk, uniformly increases during the storage period (at a slightly higher rate at 37 than at 20°), attaining the level of 9—12 μM/l after 20 weeks, i.e. a level which is more than 10 times higher in comparison with the initial values. These results favourably testify to the practical value of the Keeney and Bassette's method and, confirming their opinion, additionally throw some new light on the degree of convergence between the HMF — test and other indices of the quality of milk powder. In this connexion, the insufficient sensiblity of formol-test (in comparison with the HMF-test) results from the fact that f.ex. a decrease by only 0.1 of the percentage of formol-N, in terms of total N, when calculated for one litre of reconstituted milk, means a disappearance of $\frac{5 \cdot 0.1}{100} = 0.005$ g of free amino groups nitrogen. This value, however, constitutes $\frac{0.005}{15} \cdot 10^6 =$ about 360 μM, whereas in our case after 20 week's storage the milk powders showed only contents of 9—12 μM HMF [1] *). It results therefrom that the formol-test, in its classical execution, is unable to detect small decreases of free amino-groups in the very beginnings of Maillard's reactions, that which in so precise a manner can be measured by means of Keeney and Bassette's method.

In supplementing our results, we give some information in respect to the determination of the degree of thermal denaturation of proteins in the analyzed milk powders. The method used [5] consisted determining the ethanol-soluble fractions of proteins previonsly precipitated with the trichloracetic acid, and its results showed that the values expressed in pct. of total N were of the order of 17—19% in the stored milk powder samples of batch I, and only 15.1 to 15.5% in samples of batch II. This seems to be quite consistent with the fact that milk for the batch II (only 105°C). It also shows that in the case of batch I practically all the whey proteins have already been thermally denatured.

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*) 0.5% content of total N in milk has been assumed.

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Streszczenie

OBSERWACJE DYNAMIKI ZMIAN NIEKTÓRYCH WSKAŹNIKÓW CHEMICZNYCH JAKOŚCI PROSZKU MLECZNEGO W CZASIE JEGO PRZECHOWYWANIA

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Wykazano, że spośród kilku chemicznych testów jakości proszku mlecznego w czasie jego przechowywania, opracowana przez Kenney'a i Bassette'a próba hydroksymetylofurfurolowa (HMF) odznacza się wysoką czułością i powtarzalnością, dając możność śledzenia wczesnych stadiów przemian typu Maillarda przed wyraźniejszym wystąpieniem zmian w innych testach jakościowych.

Résumé

OBSERVATIONS SUR LES MODIFICATIONS DE CERTAINS INCIDES CHIMIQUES DE LA QUALITÉ DU LAIT EN POUDRE AU COURS DU STOCKAGE

NGUYEN HUN AT, E. PIJANOWSKI, S. ZMARLICKI (WARSZAWA)

Il a été montré que parmi plusieurs essais chimiques destiné à la caractérisation qualitative de lait en poudre stocké, la méthode mise au point par Keeney et Bassette pour le dosage de l'hydroxymethylfurfural (HMF), dont la formation résulte d'une digestion, dans des conditions standard, à l'acide oxalique, permet de contrôler, avec une précision considérable les tout premiers stades de la réaction de Maillard dans des laits en poudre stockés, avant que des modifications appréciables puissent être constatées par d'autres essais chimiques.

Summary

THE CHANGES OF SOME CHEMICAL INDICES OF NATRITIONAL VALUE OF STORED MILK POWDER

NGUYEN HUN AT., E PIJANOWSKI, S. ZMARLICKI (WARSZAWA)

It has been shown that from among several chemical tests of the quality of stored milk powder, the method devised by Keeney and Bassette for the determination of hydroxymethylfurfurol (HMF) induced in sample by standard digestion with oxalic acid enables one to control, with considerable precision, the very early stages of Maillard's reactions in stored milk powder, before any appreciable changes can be revealed by some other chemical tests.

Zusammenfassung

ÜBER VERÄNDERUNGEN EINIGER CHEMISCHER NÄHRWERTANGABEN VON MILCHPULVER WÄHREND LAGERUNG

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Es wurde festgestellt, dass unter verschiedenen Methoden zur Nährwertbestimmung von gelagertem Milchpulver, diejenige von Keeney und Bassette den Vorzug verdient. Sie beruht auf der Bestimmung von Hydroxymethyl-Furfurol (HMF), das im Versuchsmuster durch eine Normaldigerierung mit Oxalsäure entsteht und erlaubt eine genaue Kontrolle des Beginns der in gelagertem Milchpulver einsetzenden Maillard-Reaktionen, und zwar eher als andere chemische Methoden, merkliche Veränderungen hervorrufen.

Резюме

НАБЛЮДЕНИЯ ЗА ДИНАМИКОЙ ИЗМЕНЕНИЙ НЕКОТОРЫХ ХИМИЧЕСКИХ ПОКАЗАТЕЛЕЙ КАЧЕСТВА МОЛОЧНОГО ПОРОШКА В ПРОЦЕССЕ ХРАНЕНИЯ

NGUYEN HUN AT., Э. ПИЯНОВСКИ, С. ЗМАРЛИЦКИ (ВАРШАВА)

Показано, что среди нескольких химических испытаний качества молочного порошка в процессе его хранения, наиболее чувствителен метод, разработанный Кинеем и Бассеттом и основанный на реакции с гидроксиметилфурфуролом (НМГ). Этот метод, благодаря своей чувствительности и сходности результатов дает возможность проследить начальные стадии перемен типа Майярда до появления реакций в других качественных испытаниях.