HOMOGENEITY EXAMINATION OF PREMIXES AND FEEDS I

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The premixes and feeds are solid, granulous mixtures. In the course of their production the aim is — from technological point of view — to disperse the solid constituents as thoroughly as possible, i.e. to produce homogenous mixture. In fact, homogeneity of the mixture is one of the most important features of the product needed to be known not only for qualifying the mixture, but also for optimizing the technological process.

A basic requirement to homogeneity checking is to dispose over an appropriate analytical method for the examination of the composition of the samples. Since premixes and feeds are multi-component and quite complicated systems as regards their analysis, the above condition is seldom fulfilled, or not for every component. Consequently, for homogeneity examinations of premixes and feeds, often indirect methods are applied — as e.g. mixing lightly dissoluble dyestuff to the other components, dissolving the dye from the samples and determining it spectrophotometrically one can draw conclusions regarding the homogeneity of the mixture [1]. Other materials can also be applied instead of dyestuff, thus e.g. colloidal iron metal was used by American, and iron oxide by Czechoslovakian researchers to homogeneity examinations of feeds [2, 3]. These methods are, however, not ideal solutions at all, and give only approximate information regarding the homogeneity of the other components of the mixture. The individual physical characteristics of dyestuff, colloidal iron metal, iron oxide, e.g. granule size, form of granules, friction coefficient, etc. usually differ from those of the other components, thus their mixing characteristics are different, too. Therefore, if the mixture is homogeneous e.g. for the dyestuff, mixing of the other components may not be perfect with a total certainty.

Methods for homogeneity examination of premixes and feeds are known where the distribution of some actual components of the premix or feed is examined. For the investigation of feeds sodium chloride was used by Headley, while for mineral premixes Fusch and Beer analyzed the mixture by spectro-

* Phylaxia Works, Budapest X., Szállás u. 5.

photometry of copper sulfate considered as microcomponent [4, 5]. These processes dealing directly with the actual components of mixtures, provide more information about the system than do the indirect ones, although in this case too, the homogeneity to be similar to that of the other components of the mixture can only be supposed. In the homogeneity examination of some mixtures, exact information for all components of the system could theoretically only be obtained, if the examination would be extended for each component of the mixture. Since in most cases this is hindered by practical considerations, therefore those components are advisably examined which best represent the homogeneity of other components in the mixture and whose importance is the greatest in the mixture.

Preparation of mixture and mass of the samples

In the course of the examination of both premixes and feeds the basic question is how homogeneity of premixes is established and on the basis of what data.

In preparing a mixture, the substances are usually weighed according to a determined composition and the mixing is started. The composition and the weighing determine the concentration of the individual components in the mixture. During the mixing process the distribution of components tends to be perfect, the previously determined composition will be attained in ever smaller part of the mixture, i. e. the standard deviation of concentrations of the individual components becomes gradually lower in equal masses of mixture. Consequently, the concentration measured in the mixture samples, and their standard deviation, is an objective index characterizing the homogeneity of the mixture, extensively used in practice. In our work, both the concentrations of the single samples and the corrected relative standard deviations of concentrations, sampled from different points of the mixture, and their change as a function of mixing time, respectively, have been used to follow the homogenization process.

The mass of the sample is a basically important problem of homogeneity examination. The mass of the sample is mostly determined by practical considerations, mainly by the further utilization of the mixture. In the case of premixes, it means further mixing. Premix containing the essential components of the end product constitutes usually 0.5% of the feed. The capacity of the industrial mixing apparates ranges mostly from 100 to 2000 kg, thus e.g., when producing 100 kg feed, the components suitable to the prescribed composition should be contained in 500 g premixes.

For feeds, utilization is meant as direct feeding. The quantity of the daily consumed feed is various — depending on the animal species. From this

point of view, the least quantity is fed to poultry, where the homogeneity requirement is the strictest. The amount of the daily consumed feed is about 10 to 20 g.

For the chemical analysis of both premixes and feeds no sample size must be chosen where the inherent error of the measuring method causes the standard deviation of the measured concentrations to be higher by orders of magnitude than that due to inhomogeneity. For homogeneity examinations an optimum sample size is to be chosen with respect to the measuring method.

The above considerations argue for a sample size of 5 g for premixes and for 10 to 50 g for feeds.

Experimental

Examination of premixes

The premix examined consists of 18 components. Its composition is demonstrated in Table I. Concentration of the constituents was between 0.04 to 10%.

Table I

Composition of the premix

Component	%
Vitamin AD_3 product	0.32
Vitamin E	0.60
Vitamin K_3	0.04
Vitamin B_2	2.32
Vitamin B_{12}	0.40
Vitamin B_1	0.20
Vitamin B_2	0.20
Choline-chloride	11.00
Niacine	0.50
Amprolium	2.50
Zinc bacitracin	4.70
Manganese oxide	2.33
Iron sulfate	1.00
Zinc-sulfate	2.35
Cupric carbonate	0.05
Calcium iodate	0.16
Bran	71.21

Mixing apparatus: Nauta mixer with a capacity of 450 kg. The weighed materials were filled into the mixer and the mixing got started. In the course of the process, 80 to 100 g samples have been taken from the same spots of the apparatus every minute. In addition to this, during the mixing time, at $t = 2$, $t = 7$, $t = 15$ and $t = 25$ min, also samples of 80 to 100 g have been taken, this time from different spots, of the apparatus, 10 from each, which were not further homogenized. The generally used double-wall test tube has been applied for sampling [6].

Choosing an arbitrary number of the samples taken per minutes, their vitamin A and E contents have been determined. The vitamin A content of the samples, following its digestion, purification and column chromatographic separation was determined by Sobel—Werbin colour reaction, while the vitamin E content was measured spectrophotometrically [7] by Emmerie—Engel colour reaction following digestion and purification. The measuring data have been plotted vs. mixing time (Figs 1 and 2). The figure indicates the mixing time after which the state of the mixture does not change considerably and the concentration of the constituents examined approximates the value of that of the composition within about 10%. This state is reached in 8 to 10 minutes of mixing in the case of both constituents. Further on, each 10 samples taken from different spots of the mixture in the 2nd, 7th, 15th and 25th min. were examined. The iron, manganese, zinc and copper, and choline-chloride and EMQ antioxidant content were determined from the samples.

To determine the metallic components, the samples were burnt to ashes at a temperature of 550 °C, stock solution was prepared with hydrochloric acid of 10% concentration and tested in the appropriate dilutions by a Perkin—Elmer AAS instrument type 503. The EMQ (ethyl-methoxi-quinoline) content of samples was determined by fluorimetry [7] and their choline-chloride con-

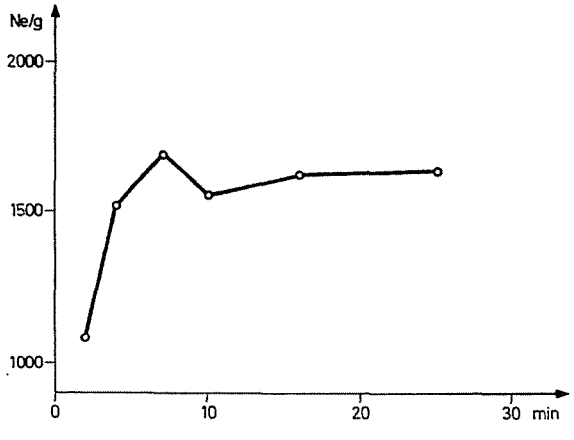

Fig. 1. Concentration of vitamin A vs. mixing time

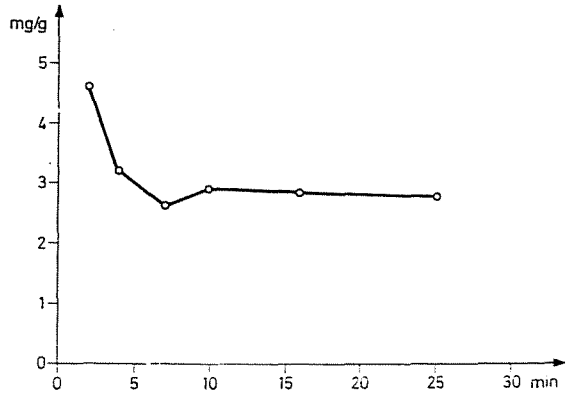

Fig. 2. Concentration of vitamin E vs. mixing time

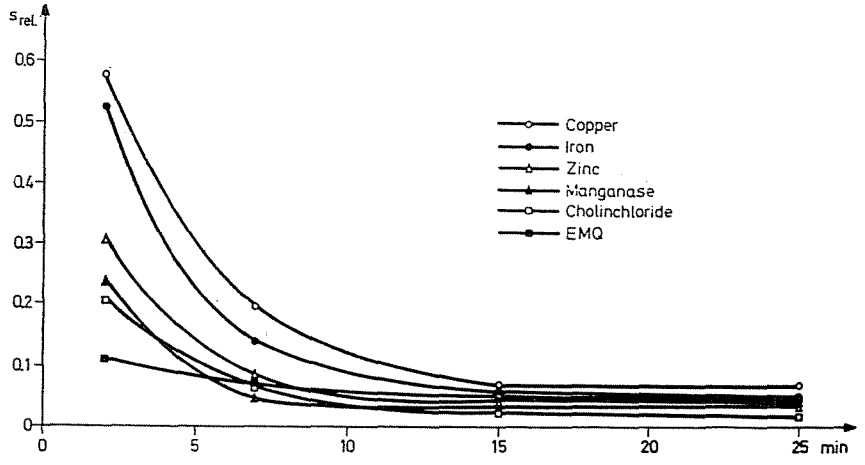

Fig. 3. Relative standard deviation of concentrations of components vs. mixing time

tent, after precipitation with Reinecke-salt, purification and dissolution, by spectrophotometry [8].

The corrected relative empirical standard deviations of concentrations have been calculated from the data of 10 to 12 simultaneous tests and plotted vs. mixing time (Fig. 3).

The following relations appear:

— the corrected relative empirical standard deviations of concentrations decrease nearly exponentially, in good agreement with theoretical considerations;

— the figure well shows the mixing time for each component, where the system has practically reached the statistically homogeneous state, at the same time also the optimum state of the system possible by mixing. After this point, it is uneconomical to continue the mixing, since the energy, work, time, expense etc. are improportional with the little qualitative improvement of the mixture. This optimum mixing time for the components examined is as follows: Cu: 14 min, Fe: 13 min, Mn: 10 min, Zn: 12 min, choline-chloride: 15 min, EMQ: 7 min.

— rapidity of mixing of the components is decisively influenced by the physical characteristics of the material, in addition to the quantitative conditions. In the mixture examined, copper was the component present in lowest concentration and reached the statistically homogeneous state almost as fast as choline-chloride, in an amount about 300 times higher than that of copper in the mixture. The basic cupric-carbonate applied is an easily mixing fine powder, while the choline-chloride is a hygroscopic, sticky material;

— importance of the operational conditions is shown by the curve of EMQ antioxidant. EMQ, the single liquid component of the mixture, is injected into the mixer during 1—2 minutes, beginning with the filling in the carrier. From among the constituents examined, the statistically homogeneous state is reached first by EMQ.

On the basis of the above, the mixing is suggested to be continued until the blending of the worst mixing component. This is mostly the component of the least grain number. It is possible, however, that not just this component will be the most hardly mixed one, since also the physical features decisively influence the speed of mixing. Thus, in the case where no experience based on concrete test results for the mixture is available, the physical characteristics of the component to be chosen for qualification are also to be taken into consideration, in addition to the quantitative conditions.

The homogeneity examination is expedient to perform also in the case of components other than those discussed above, the total distribution of which is very important from point of view of their physiological effect (e.g. essentially important or toxic materials).

Examination of feeds

In the course of manufacturing feeds, in most cases the distribution of their macrocomponents reaches quite quickly the requested degree of uniformity. In the case of feeds the problem of homogeneity is involved by the distribution of premixes present in the lowest concentration (0.5%) containing the biologically most important constituents.

During mixing, distribution of premix is followed either by examining the individual constituents forming the premix, or by determining the total

premix regarded as an "independent component". Since in the feed the concentration of the components of the premix is 200 times lower than in the premix, therefore the latter solution is easier to realize. In this case characteristics imparted the premix, should be such as to ease following distribution in the feed during mixing. Several methods have been elaborated for the problem. The present paper will report on the inactive indication technique.

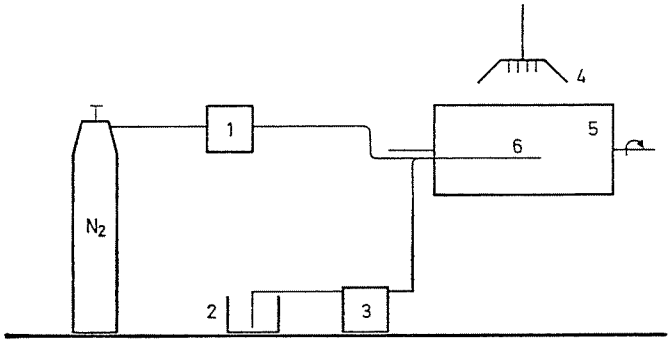

Fig. 4. Theoretical scheme of the laboratory atomizing and mixing device: 1. N_2 - preheater, 2. Solution reservoir 3. Peristaltic pump, 4. IR lamp, 5. Drum mixer, 6. Atomizer

For inactive indication a component that can be determined by properly sensitive analytical methods is to be chosen. The manganese and EMQ components of the premix were found to fit this purpose. The premix was produced in one case without manganese, and in the other without EMQ, then the manganese quantity corresponding to the composition in the form of aqueous solution, while the EMQ in its original form were sprayed upon the surface of the premix grains and left to dry. In this way, the premix contained the prescribed amounts of manganese and EMQ and differed from the usual premix only by the fact that either its manganese or its EMQ content were uniformly distributed on the surface of the other constituents of the premix. In the course of mixing, the manganese and EMQ content of samples taken from the feed showed the distribution of the premix as a "component".

A specially constructed mixing atomizer device was used for coating by manganese solution and by EMQ antioxidant. (Theoretical scheme of the device is shown in Fig. 4.).

The atomizer is operated with N_2 gas at a pressure of 0.2 to 1.5 atm, the amount of liquid to be atomized is 10 to 120 ml/hour. Capacity of the mixing drum is about 10 kg (premix). The drum can be heated with an infralamp regulated from outside, the N_2 gas can similarly be heated up to 40 to 50 °C to help the evaporation of the solvent sprayed by the tracer material. The man-

ganese sulfate was sprayed on the surface of the premix in the form of aqueous solution. In order to promote sticking to the surface, 1% gelatine was added to the aqueous solution. EMQ could directly be sprayed on the surface, it being liquid at room temperature. Uniformity of coating was controlled by determining manganese and EMQ contents of the premix samples. As for the examination of feeds, sample sizes of 10 g have been chosen, and 10 g feed contains 0.050 g premix, the uniformity of coating was checked on 0.050 g premix samples; the corrected relative empirical standard deviation of concentrations from each 10 samples was found to be:

$$s_{rel}\ (Mn) = \pm 0.07$$

$$s_{rel}\ (EMQ) = \pm 0.03$$

Distribution of manganese and EMQ content on the surface of premix constituents is seen to be adequate. In determining the Mn and EMQ content of 10 g of the feed produced with above premix, no s_{rel} values lower than the above i.e., no more homogeneous distribution can be expected.

The labelled premix was mixed together with the other components of the feed in a counter-current flush mixer. Composition of feed is given in Table II. During mixing, 10 g samples were taken each 0.5 min. from the same spot of the mixture and their manganese and EMQ content were determined. The obtained values have been plotted vs. mixing time (Figs 5 and 6), demon-

Table II

Composition of the feed

Components	%
Corn	44.0
Wheat	20.0
Bran	4.0
Soybean	18.5
Lucerne meal	2.0
Fish-meal	1.0
Meat-meal	2.8
AP-17	1.9
Lime	1.8
Salt	0.3
Aminoacid premixture	3.2
Premix	0.5

strating that after about 5 min. of mixing, the distribution of the premix in the feed becomes uniform, i.e. the homogeneity of the product cannot be significantly improved by further mixing.

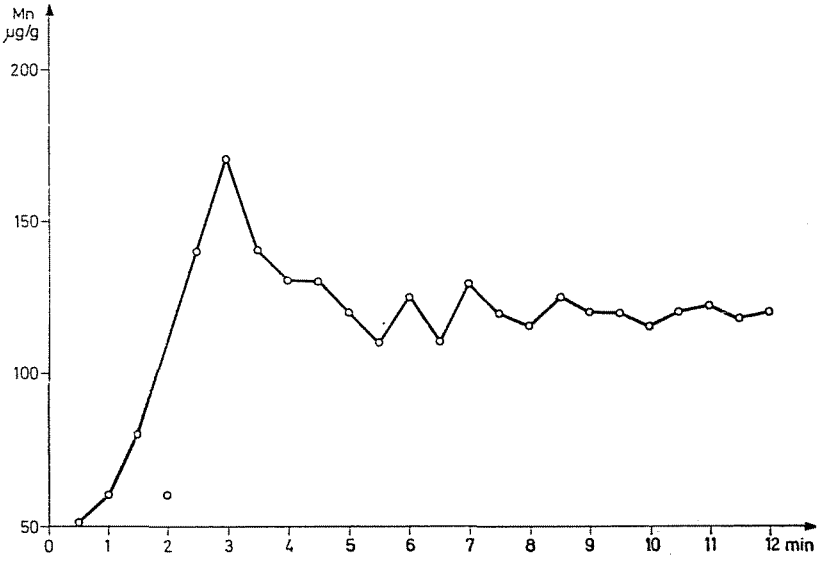

Fig. 5. Manganese content in the feed vs. mixing time

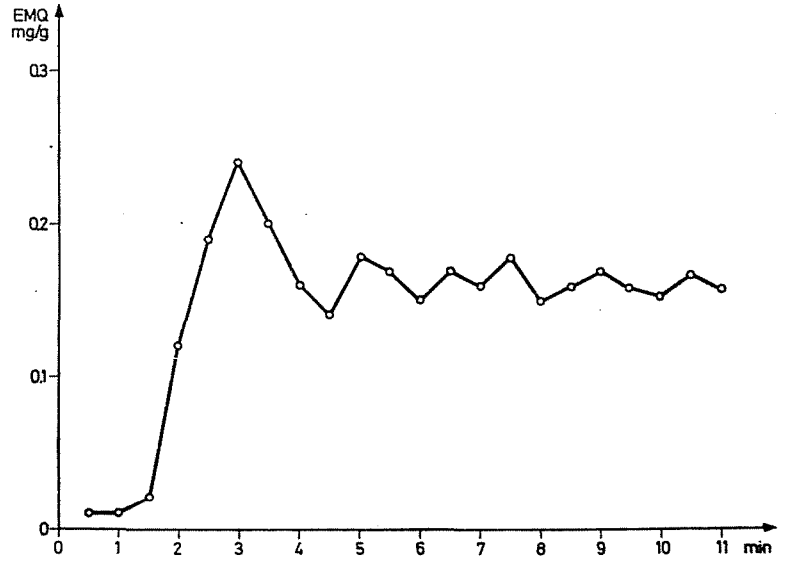

Fig. 6. EMQ content in the feed vs. mixing time

Following mixing for 5 min., the standard deviations of the change of the Mn and EMQ contents of samples are as follows:

$$s_{rel}\ (Mn) = \pm 0.05$$

$$s_{rel}\ (EMQ) = \pm 0.09$$

These standard deviations are approximately indentical to those obtained in the analysis of 0.050 g, premix samples i.e. distribution of the premix in the feed is appropriate.

Relying on the above considerations, the course of feed production can be followed so that the concentration change of the premix regarded as a labelled "component" of the feed, containing the essential constituents is examined as a function of mixing time.

Summary

Our homogeneity examination is based on the determination of the appropriate components of premixes and feeds. In the homogeneity examination of the premix, the process of homogenization could be followed by determining the active ingredients (vitamins A, E, choline-chloride, EMQ antioxidant, iron, manganese, zinc, copper) of samples taken during mixing, by observing the concentrations and the change in time of their corrected relative empirical standard deviations. In examining feeds, the premix was regarded as an independent component, and its distribution was examined by inactive indication technique. Our results offer a possibility to determine the optimum mixing time.

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