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IMPACT OF VARIOUS FORMS OF FERRIC COMPOUNDS INTRODUCED SIMULTANEOUSLY WITH VITAMINS IN FORTIFIED FLOUR

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Abstract

The study describes the development of complex groups containing iron under various forms in order to combine the latter with vitamins. The complex compositions include ferric sulphate, ferrous fumarate, elemental iron, vitamins from the B group and niacin. Flour was used as 'excipient' and was fortified with these complexes in two steps: autumnal, consisting of freshly-harvested raw material and stored when temperatures decrease; springtime, consisting of grains stored for a long time when temperatures are high.
Sensory parameters of bakery products manufactured from fortified flour made of various premixes and having passed through all different storage periods did not present any variations between one another, nor compared to control samples made of flour to which nothing was added.

***Key words**: wheat flour, ferric compounds, vitamins.*

INTRODUCTION

Research carried out worldwide with the aim to fortify food-stuff with vitamins, macro- and micro-elements for enhancing the food situation of populations has allowed for the following principles to be formulated:

1. Wisely fortifying mass-consumption food-stuff (available to all wider population groups, from children to adults consuming food-stuff on a daily basis and in all conditions) and articles of food that are refined and undergo various technological processes leading to substantial losses in micro-nutrients.
2. To fortify food-stuff, it is necessary to use vitamins and mineral matters that are known to be insufficiently consumed and/or grossly lacking.
3. The criteria for choosing a certain fortifying nutrient, its quantity and form, are: security, practicality and efficiency for enhancing the food situation of populations.
4. The amount of vitamins and mineral matters added to the products they fortify is to be considered with their natural presence in the original raw material.
5. It is essential to consider possible chemical reactions occurring when mixing various fortifying matters with the components of the fortified product; attention should be paid when choosing combinations, forms, means and steps of introducing such fortified products to ensure maximal preservation during the production and conservation processes.
6. Fortifying food-stuff with vitamins and mineral matters should not have a negative effect on the consumer properties of original products.
7. Overall consumption over 24 hours of vitamins and mineral matters should not overtake the maximum admissible amount of consumption.
8. The efficiency of adding fortifying products should receive approval and demonstrate full safety, good assimilability and capacity to substantially enhance body health through vitamins and mineral matters (Codex General Principles for the Addition of Essential Nutrients to Foods & Spirichev, 2000).

The most important micro-nutrient is iron; deficiency in iron also goes hand in hand with lack of vitamins B_1, B_2, B_6, B_9 (group B), PP.

The latter concur, at various steps, to the sorption and the metabolisation of iron in the human organism in order to ensure efficient iron assimilation (Nechaev et al.).

Flour, bread and bread-making products are food-stuff consumed on a daily basis and by all age categories of the overall population. Bread-making products are a valuable source of vitamins and mineral matters.

Wheat is the most common cereal crop: it holds PP vitamins of group B and mineral matters.

The majority of vitamins and mineral matters are concentrated in the cereal external sheath but those vitamins are lost during grinding. The lesser the flour yield is, the bigger losses in vitamins and mineral matters are.

Using more superior quality flour-based bread-making products leads to less necessary micro-nutrients (contained in such products) being assimilated by the human organism.

The most appropriate and effective way to act for ensuring enough iron to the overall population is to 'shore up' wheat flour using this micro-element. This kind of shoring-up is carried out through combining introduction of vitamins necessary for iron assimilation. Iron and vitamins quantities added to raw material need to be fixed and to be equal to physiological needs of the human organism. This allows for creating a product with guaranteed doses of vitamins and mineral matters.

Fortifying food-stuff with iron is far from being an easy task. This metal presents aliovalent impurity; it is easily catalysed through oxidation process and, especially, by processes of anti-peroxidant activity of lipids, which accelerates fats rancidification, waste flour when stored and destroy a whole series of vitamins (Suvorov et al., 2012).

Around the world, practice has led to using a vast series of vitamins and mineral matters additives for fortifiying flour and bread-making products. The following sources of iron are the most used: Fe^0 electrolytic iron; Fe^{2+} ferric sulphate and $FeSO_4 \cdot H_2O$ monohydrate; Fe^{2+} ferric sulphate and $FeSO_4 \cdot 7H_2O$ heptahydrate; $Fe(C_4H_2O_4)$ iron fumarate, $FePO_4 \times H_2O$ ferric orthophosphate; $Fe_4(P_2O_7)_3 \cdot 9H_2O$ ferric pyrophosphate.

Bioavailability of iron mostly depends of its solubility in gastric juice during digestion, of the inhibitors presence in food or the concentration of absorption-enhancing substances and of individual content in iron.

Water-soluble compounds (ferric sulfate) are instantly diluted in gastric juice and present the highest level of bioavailability. Compounds indissoluble in water (ferric fumarate) are easily absorbed because they are entirely, though slowly, diluted in gastric juice. Insoluble compounds, such as electrolytic iron, may be ill-suited to adsorption.

A repressible impact on iron absorption is exercised by compounds such as phytic acid, phenolic compounds and calcium.

To fortify flour it is necessary to select the ferric compound with the highest bioavailability, a compound that does not cause any physic-chemical and organoleptic changes in quality indicators and does not affect storage.

The objective of the present work was to focus on the impact of various forms of ferric compounds when introducing combined vitamins in fortified flour.

MATERIALS AND METHODS

A complex group was created, comprising iron under various forms in order to combine with vitamins.

The complex composition consisted in the following compounds: $FeSO_4 \times H_2O$ ferric sulphate; $Fe(C_4H_2O_4)$ ferric fumarate; Fe^0 elemental iron; vitamins from the B group (B_1, B_2, B_6, B_9); niacin (PP). Flour was used as 'excipient'.

Three types of complexes were elaborated which were stored under industrial conditions at a later stage in order to have a clear idea about the quantitative content, the compounds integrity during the storage process and to define a clear 'best-before date' for the compounds. These complexes aimed at vitaminizing flour during its making and to fortifying it when kneading dough.

Once obtained, complexes were used to fortify flour and ensure quality indicators showing a guaranteed storage life. Flour was fortified in two steps: in autumn, consisting of freshly-harvested raw material and stored when temperatures decreased; in spring, consisting of grains stored for a long time when temperatures were high.

The technological process of flour fortification consisted of the following: sieving; flour mixing to create a uniform batch; balancing; fortifying using the above-mentioned quantity of vitamins and mineral matters; mixing; packing into a tare; picking out of flour samples for monitoring storage. Storage was carried out in warehouses special chambers suitable for keeping bread-related products between 12°C and 28°C.

The formulas of premixes and dosage for flour fortification were carefully chosen in order to ensure that 30% to 40% of the human body needs were met for every 200 to 250 g of fortified-flour bread eaten.

The criteria used to evaluate the impact of those various forms of iron and vitamins on the quality of products were indicators of oxidative stability during storage on premixes and on fortified flour.

The quality of premixes during storage was monitored through the acidity index of fats contained in flour. Since flour was an integral part of premixes, it was possible to induce a degrading quality level by flour acidifying fats.

The quality indicators of the premixes and flour were determined by standard methods.

Physic-chemical and organoleptic indicators were monitored over a one-year period. Organoleptic characteristics were defined using bread that had been prepared using premixes taken out directly from dough being kneaded and fortified flour.

RESULTS AND DISCUSSIONS

The native content in iron and vitamins present in wheat grains and in flour of miscellaneous qualities (Skurikhin, 1987) is shown in Table 1.

Over the course of experimentation, iron content in mg/100 g: in a full wheat grain, 4.8 to 4.9; in siftings, 10.2 to 10.4; in low-quality wheat flour, 2.0 to 2.1; and in superior-quality wheat flour, 1.0 to 1.1. The results were in concordance with the reference data of the grain chemical content and the products derived from processing grains (Mccance and Widdowson's, 2002).

Table 1. The native content in iron and vitamins

Product	Content, mg/100 g product			
	Fe	B_1	B_2	PP
Wheat grain	5.4	0.43	0.15	5.32
Second-quality wheat flour	3.9	0.37	0.12	4.55
First-quality wheat flour	2.1	0.25	0.08	2.2
Superior quality wheat flour	1.2	0.17	0.04	1.2

When milled wheat grains lost iron from its native content; loss may reach accordingly: second-quality flour, 25%; first-quality flour, 60%; superior-quality flour, 77%. Losses in vitamins from the superior-quality flour oscillate from B_1, 60%, B_2, 70%, to PP, 66%. Data analysis showed substantive losses of native iron compounds and vitamins in the superior quality flour, which represented more than 60% of all bread-related items consumed.

To obtain the ideal quantity of easily-assimilable iron and vitamins from bread items made from first or superior quality wheat flour at a level that would not be lower than the content of a second-quality flour was possible only by using fortified flour.

Fortification of flour through adding micro-elements consisted essentially in restoring vitamins and micro-elements in the food-stuff after their elimination in the processes grains must pass through.

The composition of vitamin and mineral-matter complex is shown in Table 2.

First and superior quality flours fortified through these complex contain for every 100 g: iron, 4.1 to 5.0 mg; vitamin B_1, 0.39 to 0.47 mg; vitamin B_2, 0.12 to 0.16 mg; vitamin B_6, 0.29 to 0.31 mg; vitamin B_9, 0.040 to 0.050 mg; vitamin PP, 4.0 to 5.0 mg.

When stored, premixes present an increase in the acidity index of fats. Over 12 months, the acid index, when using elemental iron, increased by a factor of 1.6; when using ferric fumarate, by a factor of 1.1; ferric sulphate, by 1.1. Besides, the increases for both ferric sulphate and fumarate are very close; the acidification pace of a premix with elemental iron is much higher (Figure 1). Acid index of fats in all samples of premixes with various iron forms, at the outset of 12 months, is much lower than the maximal admissible value, which, for flour, is established at 50 mg/100 g of product.

Table 2. Composition of vitamin and mineral-matter complex

№	Compounds list	Quantitative composition, g/100g premix	Compounds content calculated for 1000 kg flour
Complex №1 consumption of 104 g/1t of flour			
1	Electrolytic iron (Fe^0)	28.00	29.12
2	Thiamine (B_1)	2.10	2.18
3	Riboflavin (B_2)	2.40	2.50
4	Pyridoxine (B_6)	3.00	3.12
5	Folic acid (B_9)	0.40	0.42
6	Niacin (PP)	26.96	28.04
7	Carrier – flour	37.14	–
Complex № 2 consumption of 200 g/1t of flour			
1	Ferric fumarate ($Fe(C_4H_2O_4)$)	44.18	88.36
2	Thiamine (B_1)	1.09	2.18
3	Riboflavin (B_2)	1.25	2.50
4	Pyridoxine (B_6)	1.56	3.12
5	folic acid (B_9)	0.21	0.42
6	Niacin (PP)	14.04	28.08
7	Carrier – flour	37.63	–
Complex № 3 consumption of 200 g/1t of flour			
1	Ferrous sulphate ($FeSO_4 \times H_2O$)	39.50	79.00
2	Thiamine (B_1)	1.09	2.18
3	Riboflavin (B_2)	1.25	2.50
4	Pyridoxine (B_6)	1.56	3.12
5	folic acid (B_9)	0.21	0.42
6	Niacin (PP)	14.04	28.04
7	Carrier – flour	42.36	–

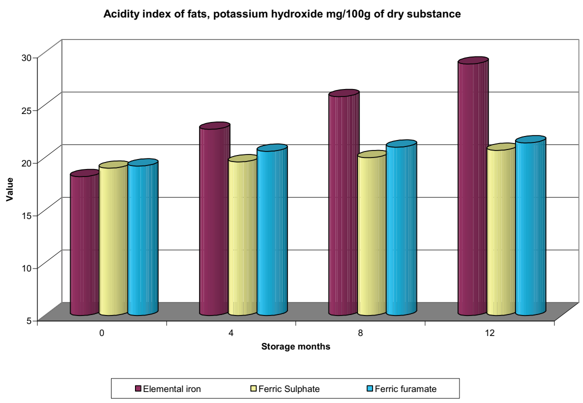

Figure 1. Changes in acid index of fats in the premixes during storage

The PP vitamins level decreased over 12 months of storage in premix with elemental iron (from 26.2% to 20.7%), with ferric fumarate (from 13.1% to 12.7%) and with ferric sulphate (from 13.2% to 12.0%). PP vitamins level of preservation with elemental iron was 79%; with ferric fumarate, 97%; with ferric sulphate, 91%. The sharpest decrease in PP vitamins level was observed in the premix with elemental iron (Figure 2).

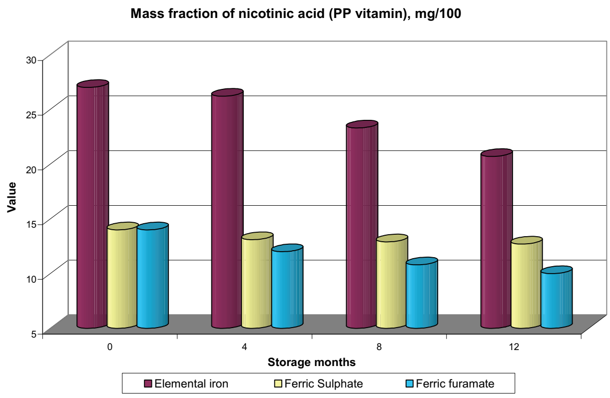

Figure 2. Changes in nicotinic acid content in the premixes during storage

Folic acid content during storage (Figure 3) remained almost unchanged when laying premix with elemental iron; folic acid level decreased by 19% with ferric fumarate; and by 24% with ferric sulphate.

Organoleptic indicators in the bread made of premixes directly added when kneading dough showed that the bread quality did not depend on how many months the premixes were stored; besides, there was no change in flavour, taste, aroma, crumb condition. Bread samples were not marked by any change according to physic-chemical indicators.

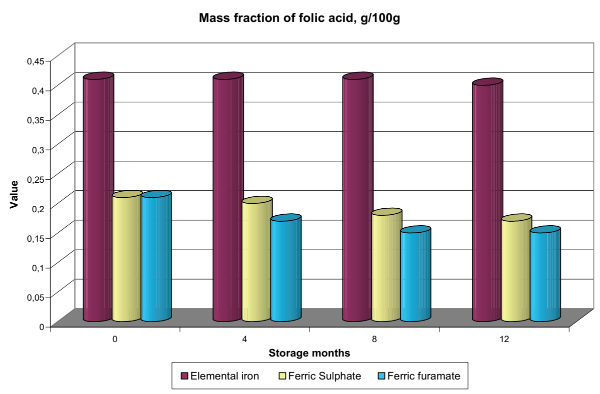

Figure 3. Changes in folic acid content in the premixes during storage

Hence the present research allowed establishing that the various forms of iron used for creating compounds presented a negligible impact on quality indicators and components preservation when the product was stored for one year. This allows for the use of the said iron forms aiming at flour fortification over a one-year period.
The autumnal-stored flour was kept for 12 months; the spring-stored flour, for 6 months. The humidity change in flour was not identified. Over the first 6-month storage period, humidity decreased and then (for fortified autumnal flour) increased (Figure 4). In this regard, it was necessary to emphasize that all samples analysed during the storage process met the requirements (Codex Standard FOR Wheat Flour), namely a maximum of 15.5%: samples displayed 12.0% to 13.0% for autumnal fortified flour and 13.6% to 14.4% for spring flour (Figure 5).
In the autumnal (spring) fortified flour, the water impact over the course of storage was the following: control, 0.46 to 0.57 (0.54 to 0.55); with elemental iron, 0.47 to 0.57 (0.57 to 0.61); with ferric fumarate, 0.55 to 0.57 (0.58 to 0.60); with ferric sulphate, 0.43 to 0.57 (0.59 to 0.60) and then the characteristic modifications were correlated with the modifications caused by product humidification (Figure 6).
Acidity index of fats for wheat flour, in conformity with (Codex Standard for Wheat Flour) was standardised at 50 mg potassium hydroxide /100 g of dry substance.

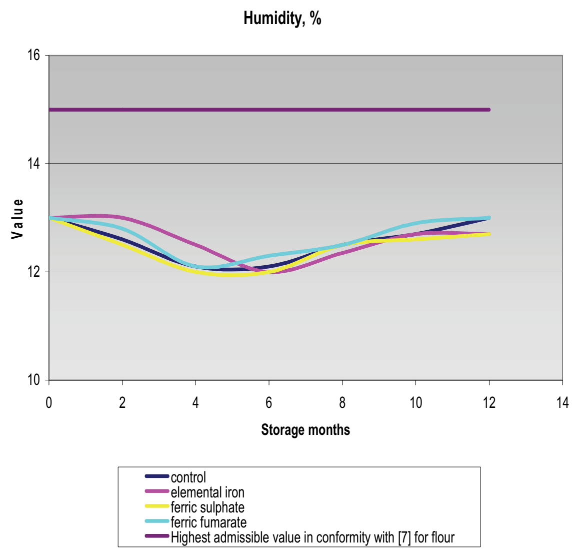

Figure 4. Humidity of the autumn-fortified flour during storage

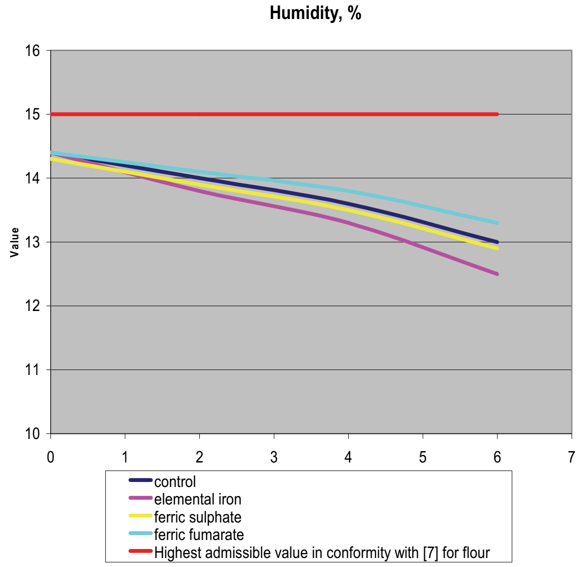

Figure 5. Humidity of the spring-fortified flour during storage

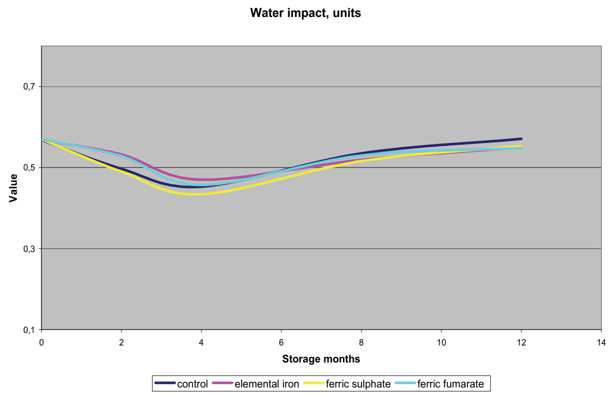

Figure 6. Water activity of the autumn-fortified flour during storage

The acidity index present increased fat levels in the experimental samples and control samples (Figure 7 and Figure 8).
Over 12 months of storage the acidity index of fats showed increased indicators for autumnal fortified flour: the control sample increased by 2.5 times, experimental samples by 2.2 to 2.3 times. Moreover, a lesser increase was noticed in terms of the fats acidity index of premixes with ferric sulphate and elemental iron (respectively, 34 mg of potassium hydroxide/100 g of flour and 35.9 mg/100 g); a bigger increase is noticed in the control sample and in the premix with ferric fumarate (respectively, 36.9 mg of potassium hydroxide/100 g of flour and 37.4 mg/100 g).

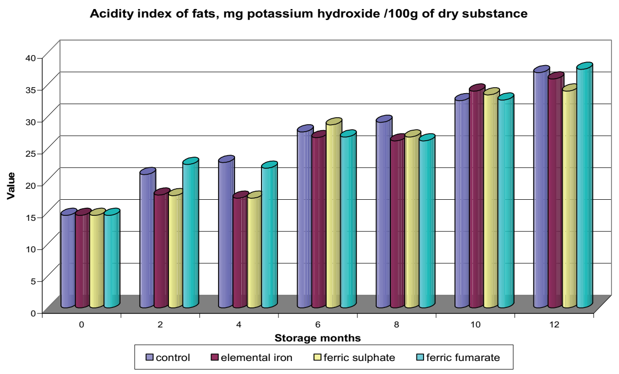

Figure 7. Acid index of the autumn-fortified flour during storage

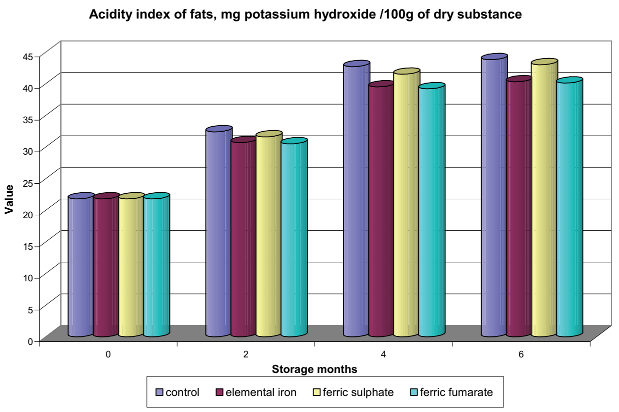

Figure 8. Acid index of the spring-fortified flour during storage

Concerning spring-fortified flour of the beginning of the storage period, when temperatures increased rapidly, the fats acidity index also rapidly increased from 24.1 to 42.7 mg of potassium hydroxide/100 g of dry substance; besides, this indicator increased in the control sample, as well as in all other experimental samples.

In all samples, the potassium hydroxide levels were much lower than the regulatory standard applied to autumn fortified flour, and lower than the admissible value for spring-fortified flour. As for the control sample, the fats acidity index did not exceed 65% (85%) of the regulatory standard. For autumn-fortified and spring-fortified flours, respectively: ferric sulphate, 66% (86%); ferric fumarate, 65% (82%), elemental iron, 68% (81%).

The nicotinic acid mass fraction presented negligible variations during the storage process; it remained at the same level in experimental and control samples.

Organoleptic characteristics in bread-making items produced from fortified flour made of various premixes and having passed through all different storage periods presented no variations, compared to one another and the control samples made of flour to which nothing was added.

Fortification of flour using premixes enriched with vitamins and mineral matters may be carried out in flour-milling plants, as well as while kneading dough during the bread-making process.

Flour production in milling plants included magnetic traps as the last step before prepacking. Consequently, premixes with elemental iron could not be used; nevertheless, other kinds of premixes could replace them successfully.

When fortifying flour at the kneading-dough step, all kinds of premixes can be used.

Economy is a crucial factor when choosing which premix to use for fortifying flour.

Our point of view on fortified flour storage in unregulated conditions is that storing term should not exceed 12 months in the case of autumn-fortified flour and 6 months in the case of spring flour.

CONCLUSIONS

The results of our experiments are the following:

1. Elaboration of three kinds of compounds aiming at fortifying flour through the use of various forms of iron and vitamins that concur to enhance their assimilation by the human body.

It has been established that the studied forms of iron used for creating compounds have a negligible impact on quality indicators and preservation of premix compounds when stored for about one year.

- a negligible increase in the fats acidity index is observed; this increase has no impacts on organoleptic indicators of fortified flour and the products based upon it.
- the highest preservation rate of folic acid is observed in premixes with elemental iron and the lowest rate, with ferric sulphate.
- a high preservation rate of PP vitamin is observed in all kinds of premixes during the storage process.

2. Fortification of flour has been carried out, including its following storage in unregulated temperature conditions over a two-step period:

autumn (beginning with a fall in temperatures and then a rise) and spring (with a rise in temperatures in the beginning followed by a fall).

It has been established that acidification processes happening in flour are more active during spring fortification, not only in fortified flour but also in control premixes devoid of additions:

- the acidity index of fats rate exceeds 12% to 19% correspondent values of fortified flour when stored in autumn.
- the lowest rate of acidity index of fats is observed in the flour fortified using elemental iron.
- over one year of storage of autumn-fortified flour and 6 months of spring flour no essential changes are observable in terms of quality and organoleptic indicators; those fortified flours do not differ from one another, nor from control flour devoid of additions. This shows that it is possible to fortify flour using the elaborated said compounds.

3. The choice of a premix may be conditioned by technological processing of grains, the production of flour and economic considerations.

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