PRESERVATION OF CHEMICAL PARAMETERS IN CEREAL GRAINS STORED IN NITROGEN

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ABSTRACT

Soft wheat and maize at various moisture contents were stored in experimental and pilot scale silos in air and technical or pure nitrogen. Samples of cereal grains and wheat flour were chemically analyzed throughout the storage periods for the main quality parameters.

The results have shown that preservation in nitrogen, especially at higher moisture contents, has a protective effect, permitting satisfactory storage for longer periods than by traditional preservation methods.

INTRODUCTION

During storage, wheat is subject to changes that are not only due to biotic factors, but also to physico-chemical phenomena indipendent fromthe first, although often related to them.

Among the chemical components of wheat, the lipids are the most susceptible to alterations during maturation and storage of the product itself or of the flour (MacMurray and Morrison, 1970).

Storage of cereals and of their derived products implies lipid changes due to oxidation and hydrolysis processes (Moran et al., 1954) resulting in the increase of the acidity degree. Oxidation effects the double bonds of the fatty acids in the lipid molecule; the unsaturated fatty acid content thus determines the storage alterations reflected by the physical, organoleptic and technological characterisatics of cereals and their derived products.

The incidence of these phenomena depends first of all on storage conditions and particularly on the moisture content (Cucudet et al., 1954) and temperature (Glass et al., 1959) of storage.

Since this subject has a great importance, we thought it necessary to pay particular attention to the investigation of the possible wheat lipid changes at different moisture contents during storage in nitrogen atmosphere.

MATERIALS AND METHODS

Soft wheat of different varieties and Goliath maize were tested at natural and artificially raised moisture contents for their storability in nitrogen versus oxygen containing atmospheres (Shejbal, 1979).

Samples of wheat and its flour, and maize, were analyzed throughout the storage periods, with special regard to:

1. Viability
   1.1 Germination energy
   1.2 Germination capacity
2. Determination of proteins
   2.1 Total proteins
   2.2 Gluten quantity
   2.3 Gluten quality
3. Determination of sugars (according to AAC methods)
   3.1 Reducing sugars
   3.2 Non reducing sugars
4. Lipid characterization (according to AACC methods and Carnovale and Quaglia, 1973)
   4.1 IR spectra of acetone extracts
   4.2 Acidity index
   4.3 Fatty acid composition of ether extract
   4.4 Determination of tocopherol content.

RESULTS AND DISCUSSION

Long-term storage of dry soft wheat

Two samples of soft wheat, "Conte Marzotto" variety, at an initial moisture content of 10.5%, were stored in minisilos in air and in technical nitrogen for 5 years. Storage temperature was 18°C in winter and 32°C in summer.

During the second year the wheat moisture content was increased to 12%, a level closer to that currently present in national wheat.

Table 1 shows that germination capacity remained high during the first 3 years in both samples; during the fourth year, and particularly in the last months of the experiment, germination capacity decreased significantly in air stored wheat, but remained high in nitrogen stored wheat.

Gluten quality was reduced in both wheat stored in air and nitrogen, but air storage had a greater adverse effect.

These results show that wheat stored in partial absence of oxygen remains unaltered during a far longer period of time than that required in Italy for commercialization.

Because of the encouraging results obtained in minisilos we considered it necessary to repeat the experiment under the same conditions on pilot scale.

Dry soft wheat storage in a pilot scale plant

Table 2 shows the chemical and biological data of wheat "Conte Marzotto" at a low moisture content and derived flour at trial start and after 58 weeks. It seems that during the storage period no significant change occurred either in the wheat or its flour. Only the acidity degree expressed by the fatty acid index (FAV) showed a slight increase.

Table 3 shows analogous results for flour demonstrating that I.R. absorption of -COOH groups has the same trend as FAV in the whole wheat.

These results confirm the possibility of employing such a storage technique for dry soft wheat.

Table 1 - Storage of soft wheat "Conte Marzotto" in air and in nitrogen

Parameters	Time (years)						
	0	3		4		5	
		air	nitrogen	air	nitrogen	air	nitrogen
Moisture content (%)	10.5	12.2	11.9	12.5	12.3	12.7	12.3
Germinative capacity (%)	96	93	93	75	87	4	87
Gluten (% d.m.)	11.3	10.1	10.2	10.1	9.9	9.4	9.3
Gluten quality	excellent	good	excellent	short	good	short	good

Table 2 - Storage of soft wheat "Conte Marzotto" on pilot scale in technical nitrogen for 58 weeks

Parameters	Time "O"	58 weeks
Moisture content (%)	10.5	10.5
Total proteins (Nx5.70) (% d.m.)	14.0	13.4
Gluten (% d.m.)	10.1	10.1
Reducing sugars (mg maltose/10 g)	26	38.3
Non reducing sugars (mg sucrose/10g)	185	215
Germinative capacity (%)	99	99
FAV units	23.0	25.2

Table 3 - Chemical features of flour obtained by industrial milling of soft wheat "Conte Marzotto" stored in nitrogen for 58 weeks

Parameters	Time "O"	58 weeks
Moisture content (%)	13.7	13.9
Total proteins (Nx5.70) (% d.m.)	13.1	13.1
Reducing sugars (mg maltose/10 g)	21	15.1
Non reducing sugars (mg sucrose/10 g)	137	152.7
Gluten (% d.m.)	10.4	10.1
A (-COOH) U.A.	0.42	0.48

In order to evaluate the possibility of applying nitrogen atmospheres to the storage of wheat with a higher moisture content, tests were carried out on soft wheat with a moisture content above 14.5%, a value at which serious storage problems, even for short periods, arise in Italy.

Soft wheat storage at critical moisture content

Soft wheat "Cappelle" variety, at 14.5% moisture content was stored in mini-silos in air and in technical nitrogen, with 0.2% of oxygen, for 32 weeks. The temperature was 18-20°C during the first 20 weeks, and at trial end, in the summer, it reached 26°C.

Germination capacity of wheat stored in air and in nitrogen did not show any noticeable variation during the experiment, only a slight increase of the acidity degree, with a FAV enhancement could be demonstrated (table 4).

Table 4 - Storage of soft wheat "Cappelle" at critical moisture content in air and in technical nitrogen for 32 weeks

Parameters	Time "0"	Air	Nitrogen
Moisture content (%)	14.5	14.5	14.3
Total proteins (Nx5.70) (% d.m.)	12.4	12.0	12.4
Germinative capacity (%)	93	91	93
FAV units	26	33	32

Results reported in table 5 on chemical parameters in the flour obtained from the wheat, do not show any significant difference in gluten and surgar between flours obtained from the samples stored in air and in nitrogen.

Flour from air stored wheat seems to indicate that during storage a slight lipo-oxidative process has taken place, whereas no such phenomenon appears to have affected the nitrogen stored wheat. In fact this is shown by the data reported in table 6, where the increase of the acidity degree during 32 weeks of storage, as revealed by I.R. absorp-

Table 5 - Chemical features of soft wheat "Cappelle" flour at critical moisture content stored in air and in technical nitrogen for 32 weeks

Parameters	Air	Nitrogen
Gluten (% d.m.)	8.7	8.8
Gluten quality	very good	very good
Reducing sugars (mg maltose/10 g)	23	27
Non reducing sugars (mg sucrose/10 g)	160	172

Table 6 - Free fatty acids percent composition of flour obtained from wheat at the beginning (time"O") and after 8 months storage in air and in nitrogen

Analysis	Time "O"	After 8 months storage	
		dry wheat in air	dry wheat in nitrogen
Palmitic acid (16:0)	23.9	23.5	24.3
Stearic acid (18:0)	1.4	tr	tr
Oleic acid (18:1)	8.8	10.9	8.8
Linoleic acid (18:2)	61.3	52.1	62.9
Linolenic acid (18:3)	4.5	10.1	3.7
Arachidonic acid (20:4)	tr	3.2	0.3
$R = \frac{\text{unsaturated}}{\text{saturated}}$	3.0	3.2	3.1
A (-COOH) U.A.	0.22	0.32	0.30

tion of -COOH moiety, appears to be higher in air stored wheat. In this same wheat, linoleic acid decreases in air, proving thus that an oxidative process occurs. This does not take place in the nitrogen stored wheat, where the fatty acid composition remains almost the same as that of flour derived from wheat milled at the start of the trial.

Soft wheat storage at overcritical moisture content

Since soft wheat storage at overcritical moisture content might be of great practical value, we decided to proceed to 3 test series with artificially moistened wheat.

Our experiment was carried out on different wheat varieties, i.e. Marzotto and Cappelle as an example of Italian and French medium force wheat, and Red Spring as an example of force wheat. Samples were moistened, by repeated additions of distilled water and successive mixing, to a level of 17.4%, 18.0% and 17.5% respectively.

Each wheat sample was stored in minisilos, in air and in technical nitrogen, for 32 weeks.

Germination capacity of moistened wheat decreases more rapidly in air than in nitrogen: after 10 weeks storage in air it reaches 55%, and 70% if stored in nitrogen. At the end of the experiment it reached 0 level for all the samples (table 7).

Also the fat acidity value (FAV) shows a greater increase when wheat is stored for 10 weeks in air than in nitrogen, this difference is confirmed at trial end (table 7).

No change in protein content was demonstrated.

Gluten quantity of flour from wheat stored in air proved to be less than that of the wheat stored in nitrogen, although both suffered a quality deterioration. Reducing sugars increased more in air than in nitrogen stored wheat, while the non-reducing sugars experienced a reduction from their initial value of 232, 270, 288 mg sucrose 10 gr dry weight for Cappelle, Manitoba, Marzotto respectively (table 8).

Table 7 - Storage of three varieties soft wheat at over critical humidity in air and in technical nitrogen for 32 weeks

Parameters	Cappelle			Red spring			Marzotto		
	Time 0	Air	Nitrogen	Time 0	Air	Nitrogen	Time 0	Air	Nitrogen
Moisture content (%)	17.4	18.0	17.0	18.0	18.0	17.8	17.5	17.5	17.1
Total proteins (Nx5.70) (% d.m.)	12.4	12.3	12.0	12.4	12.2	12.3	12.0	11.9	12.0
Germinative capacity (%)	94	0	0	88	0	0	88	0	0
FAV units	30	47	42	37	91	46	32	36	42

Table 8 - Chemical features of flour from three varieties of soft wheat at over-critical moisture content, stored in air and in nitrogen for 32 weeks

Parameters	Cappelle		Red spring		Marzotto	
	air	nitrogen	air	nitrogen	air	nitrogen
Gluten (% d.m.)	6.7	7.3	10.7	10.6	6.6	7.1
Gluten quality	short	short	short	short	short	short
Reducing sugars (mg maltose/10 g)	64	48	148	148	108	80
Non reducing sugars (mg sucrose/10 g)	123	142	92	90	150	188

Table 9 shows the free fatty acid composition of the flour lipidic extract. The unsaturated saturated fatty acid ratio indicates that this index does not change with time in the nitrogen stored moist wheat, but it appears to become twice as high in the air stored wheat, where hydrolysis takes place.

I.R. analysis of the acetonic extract provides a further evidence by showing that especially the air stored wheat exhibits an absorption change in the area characteristic for the -COOH moiety (table 9).

Table 9 - Free fatty acids percent composition of flour obtained from "Cappelle" at over critical humidity stored in air and in technical nitrogen for 32 weeks

Analysis	Time "O"	Air	Nitrogen
Palmitic acid (16:0)	23.9	15.3	26.0
Stearic acid (18:0)	1.4	tr	tr
Oleic acid (18:1)	8.8	9.3	10.5
Linoleic acid (18:2)	61.3	70.6	60.0
Linolenic acid (18:3)	4.5	4.7	2.8
Arachidonic acid (20:4)	tr	tr	0.7
$R = \frac{\text{unsaturated}}{\text{saturated}}$	3.0	5.5	2.8
A (-COOH) (U.A.)	0.22	0.71	0.36

Wet harvested maize storage

Maize at 18-19% moisture content was stored in nitrogen and air at external ambient temperatures in mini-silos from autumn to spring and in microsilos at 21 $\pm$ 1°C for over 20 weeks.

As can be seen in fig.1, at ambient external temperatures, the absence of oxygen did not permit any substancial increase in fat acidity, neither in a pressurized silo (P) nor under nitrogen flow (F), due to the virtual absence of moulds. At the same time, however, some carbohydrate transformation took place, shown by the decrease in nonreducing

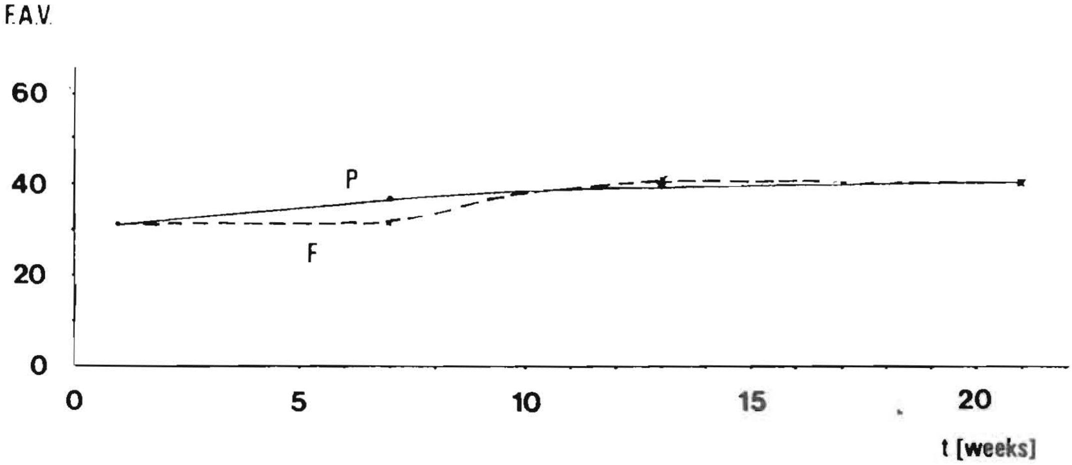

Fig.1. Evolution of fat acidity in wet harvested maize stored at ambient temperature in nitrogen flow (F) and in a pressurized mini--silo (P).

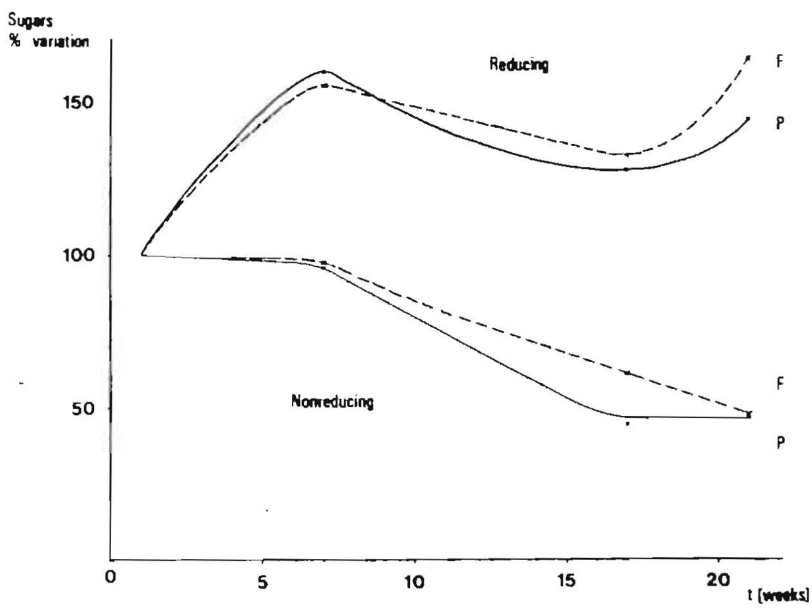

Fig.2. Evolution of reducing and nonreducing sugar content in wet harvested maize stored at ambient temperature in nitrogen flow (F) and in a pressurized mini-silo (P).

sugars, due to the moisture content dependent activation of the respective enzymes (fig.2).

At a constant temperature of 21°C, the effect on fat acidity was similar as in the preceding experiment, as far as nitrogen preservation was concerned. In pressurized airtight microsilos in air, a high concentration of carbon dioxide was soon reached, moulds (except Candida) were largely inhibited and therefore, here too, fat acidity did not increase (fig.3).

On the contrary, in microsilos, in which some air was added regularly (because of a leak of the pressurized silos), moulds proliferated freely and fat acidity increased accordingly.

As can be seen in fig.4, the effect of the various gas conditions on carbohydrates is not very much pronounced, the enzymes involved in their transformation not being oxygen dependent. The decrease in reducing sugars is due to them being consumed by proliferating moulds.

The separation of starch from proteins was not affected by storage in anaerobic conditions, while it was largely impaired in air storage.

It is, of course, impossible to maintain viability for long periods of time at moisture contents as high as 18-19%. In fact, it decreased rapidly already during the first four weeks of storage even in nitrogen, although slower than in air.

The results show that the limiting factor of moist maize preservation in controlled atmospheres is the presence, even of small amounts, of oxygen, which permit mould growth.

CONCLUSION

The storage experiments on maize and various wheat varieties with different moisture contents and for different storage periods have proved the advantages of technical nitrogen, particularly when moisture content is overcritical. Nitrogen atmosphere allows prolonged storage without need of the common disinfesting drugs or other protective treatments. Storage is however limited in time by mould proliferation, the development rate of which is slowed down, although not totally inhibited, when oxygen is present at 0.2 to 0.5% as is the case of technical nitrogen.

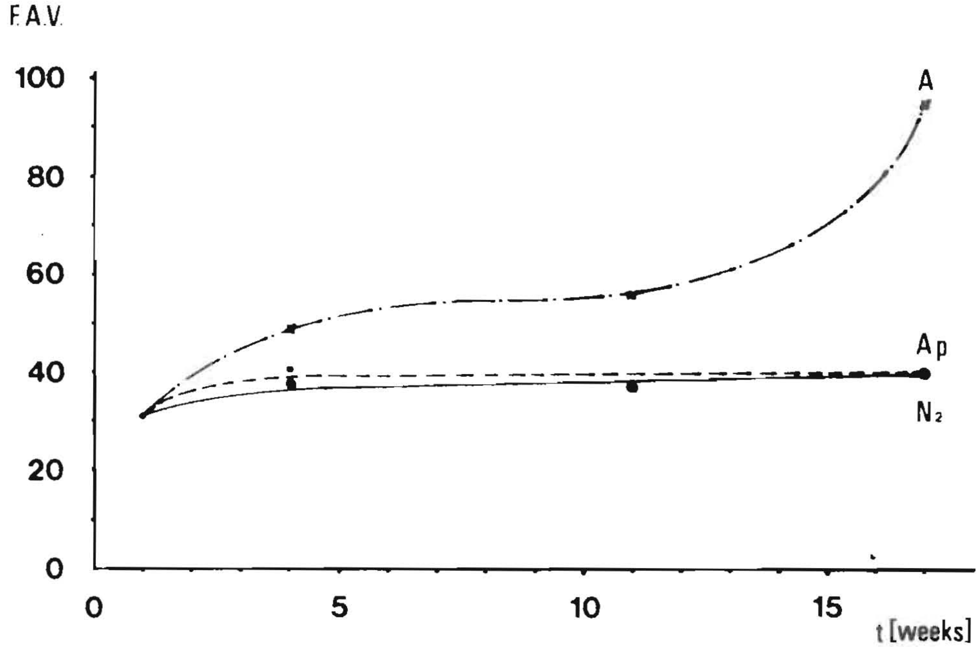

Fig.3. Evolution of fat acidity in wet harvested maize stored at 21°C in micro-silos under nitrogen (N_2), confined atmosphere (Ap) and with regular additions of air (A).

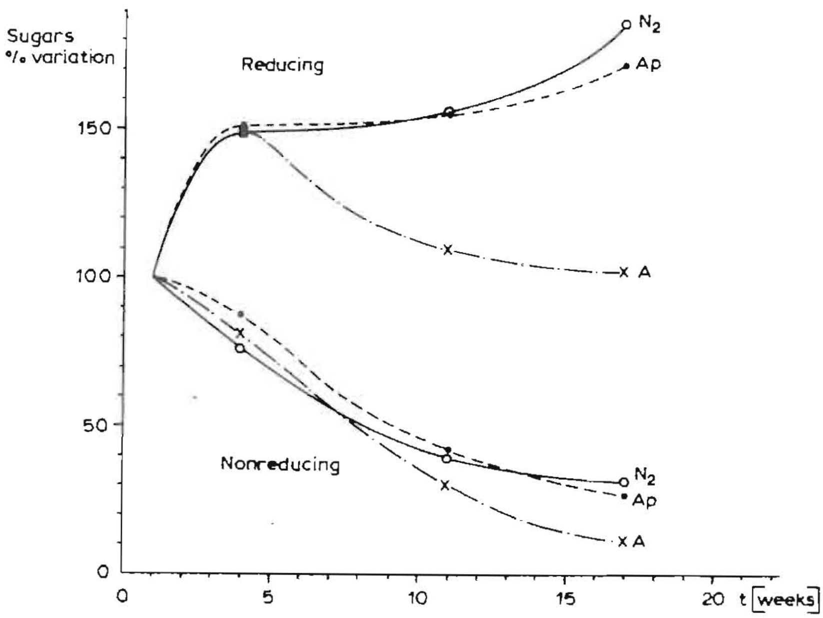

Fig.4. Evolution of reducing and nonreducing sugar content in wet harvested maize stored at 21°C in micro-silos under nitrogen (N_2), confined atmosphere (Ap) and with regular additions of air (A).

REFERENCES

American Association of Cereal Chemists, 1969. Cereal Laboratory Methods.

Baker, D., Neustadt, M.H. and Zeleny, L., 1957. Application of the fat--acidity test as an index of grain deterioration, Cereal Chem., 34: 226-233.

Carnovale, E. and Quaglia, G.B., 1973. Effets de la conservation a température et humidité controlées sur la composition chimique des produits de moisture du mil, Ann. Technol. Agric., 22: 371 - 380

Cucudet, L.S., Larson, E., Norris, S.G. and Geddes, W.F., 1954. The influence of moisture content and other factors on the stability of wheat flours at 37,8°C, Cereal Chem., 31: 362 - 389

Glass, R.L., Ponte, J.G., Christensen, C.M. and Geddes, W.F., 1959. The influence of temperature and moisture level on the behavior of stored in air or nitrogen, Cereal Chemistry, 36: 341 - 350

Lombardi, M., Quaglia, G.B. and Shejbal, J., 1976. Effetto della conservazione di frumento tenero in azoto sulle caratteristiche tecnologiche. Tec. Molitoria, 27: 97-103.

MacMurray, T.A. and Morrison, W.R., 1970. Composition of wheat-flour lipids, J. Sci. Fd. Agric., 21: 520-528.

Moran, C.B.E., Pace, J. and McDermott, E.E., 1954. Oxidative changes induced by storage and improver treatment, Nature, 174: 449-452.

Shejbal, J., 1979. Preservation of cereal grains in nitrogen atmospheres. Resource Recov. Conserv., 4: 13-29.