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Minerals

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SUMMARY

Minerals

The possible changes in the mineral composition of food during frying could be the consequence of losses by leaching, or changes in concentrations caused by exchanges between the food and culinary fat of other compounds. The net result depends on the type of food, the frying fat used and the frying process. Moreover, the modifications that frying produces in other nutrients could indirectly affect the availability of dietary minerals. The most outstanding ones are those that can take place in the fat or in the protein. With respect to the interactions between frying oils and minerals, we have recent knowledge concerning the effects of consuming vegetable oils used in repeated fryings of potatoes without turnover, on the nutritive utilization of dietary minerals. The experiments have been carried out in pregnant and growing rats, which consumed diets containing, as a sole source of fat, the testing frying oils or unused oils. It seems that the consumption of various frying oils, with a polar compound content lower or close to the maximum limit of 25% accepted for human consumption, does not alter the absorption and metabolism of calcium, phosphorous, iron or copper. Magnesium absorption from diets containing frying oils tends to increase but the urinary excretion of this element increases, resulting imperceptible the variations in the magnesium balance. The urinary excretion of Zn also increased although its balance remained unchanged. Different studies referring to the effects of consuming fried fatty fish on mineral bioavailability will also be presented. On one hand, frying can cause structural changes in fish protein, which are associated with an increase in iron absorption and a decrease in body zinc retention. The nutritive utilization of other elements such as magnesium, calcium and copper seems to be unaffected. On the other hand, it has been described that an excess of fish fatty acids in the diet produces iron depletion, but when fatty fish is fried in olive oil the quality of the fish oil improves, enhancing the nutritive utilization of iron and other dietary minerals.

KEY-WORDS: Bioavailability – Fried fish – Frying oil – Minerals.

INTRODUCTION

Minerals are very stable under high temperature conditions. It is known that heating does not destroy minerals, at least as far as 400ºC and ashing is a normal procedure for the analytical determination of these inorganic food components. Therefore, the thermal treatment that takes place during frying does not affect the chemical element, although it can be said that, in an indirect way, frying can positively or negatively modify the nutritive utilization of the minerals of in diet.

Minerals which can be found in food have been clasified in two cathegories: major minerals (Na, K, Mg, Ca, P and Cl) and trace elements (Fe, Zn, Cu, Se, I, Cr, Mn, Mo, Co, As, Ni, Si, F, B, V). However, on one hand considering some of the ultratrace elements as essential is controversial at present, on the other hand more elements will be added to the above list in a near future (Nielsen, 1994). Minerals have structural as well as regulatory functions in the body. Depending of their chemical properties, interactions between minerals or between minerals and other food components may occur. These interactions may take place at absorption or metabolic stages. The physiological consequences of these interactions may involve decreasing of the bioavailability of one or various minerals.

Due to the fact that most food is not consumed raw but cooked, it is important to know the characteristics of the interactions between minerals and other food components in ready to eat meals and specially the effects on the absorption and metabolic utilization of minerals. In this report the possible influence of frying on the bioavailability of several minerals will be examined, assuming that bioavailability is the proportion of the total mineral in a diet that is utilised for normal body functions (Fairweather-Tait, 1992).

1. CHANGES IN THE MINERAL COMPOSITION OF FOOD BY FRYING

The process of frying involves dehydration, which is higher than in other cooking processes. Therefore, when we eat fried food we eat a product with a higher nutrient density than in its raw state. This applies also to minerals, as shown in Table I comparing raw sardines with sardines fried in olive oil. However, there is no total agreement on this point. Several authors have indicated that the variations in the mineral composition of fish due to frying are rather small (Causeret, 1962; Moreiras-Varela *et al.*, 1988). Others (Gall *et al.*, 1983) have reported that frying fatty fish does not cause quantitative changes in sodium, calcium, phosphorous, magnesium, iron, zinc, copper and manganese while frying low-fat fish produces slight losses of sodium, potassium and magnesium, although several trace elements do not vary (Fe, Zn, Cu and Mn) (Gall *et al.*, 1983).

Table I
Composition of raw and fried sardines (g/100g of fish)

	Moisture	Protein	Fat	Ashes
Raw sardine	60.7 ± 0.3	20.7 ± 0.6	15.4 ±0.1	3.3 ± 0.1
Fried sardine	43.1 ± 0.8*	32.3 ± 0.5*	21.2 ± 0.1*	5.4 ± 0.1*

*, $p < 0.05$
(From Alvarez-Pontes, 1994)

Expressed on a dry basis, Mondy and Ponnampalam (1983) found reductions of particular minerals in fried potatoes, which were attributed to the possible increase in cell separation of the cooked tissues or to the leaching of minerals into fat medium.

Considering the data obtained with different kinds of food subjected to frying, it seems that food with low fat content and high water content are more susceptible to lose minerals than fatty food. But from the practical point of view this may not be very relevant since the concentration of minerals in fried food is relatively high compared to other cooking practices.

2. USED FRYING OILS CONSUMPTION AND BIOAVAILABILITY OF DIETARY MINERALS

2.1. Interaction type of fat-minerals:

The information concerning the influence of minerals on lipid metabolism is well documented but there is little knowledge on the opposite influence. The quantity of dietary fat as well as its saturation degree, fatty acid chain length and triglyceride structure may affect mineral bioavailability.

Calcium is absorbed better with short chain fatty acids than long chain fatty acids and with unsaturated compared to saturated fatty acids (Kies, 1985). Therefore, an increase in the unsaturated/saturated fatty acid ratio enhances calcium absorption if the chain length is not very large. For example, erucic acid (C22:1) decreases calcium absorption while oleic acid (C18:1), which is also a monounsaturated fatty acid but with a shorter chain, stimulates it (Laval-Jeantet and Laval-Jeantet, 1976, Navarro *et al.*, 1980). In this line, high intakes of estearate and palmitate have been shown to reduce calcium absorption (Allen, 1982).

Growing rats that were fed diets containing olive oil or sunflower oil as the only dietary fat showed that both oils exert a similar influence on the nutritive utilization of phosphorous (Pérez-Granados *et al.*, 1993) and magnesium (Navarro *et al.*, 1993). The efficiency of calcium absorption tended to increase with sunflower oil compared to olive oil, which is likely due to the different levels of linoleic (C18:2) and oleic (C18:1) acids in these oils, being more unsaturated the first one. Nevertheless, this influence on the absorption stage was not very intense since the net absorption of calcium and the calcium balance did not vary (Navarro *et al.*, 1993).

In contrast to calcium, iron metabolism is negatively affected by polyunsaturated fatty acids compared to saturated fatty acids (Lukaski *et al.*, 1982; Rao *et al.*, 1983; Van Dokkum *et al.*, 1983; Johnson *et al.*, 1987). Consumption of polyunsaturated fatty acids from the n-3 series by rats (fish oil as the only dietary fat) causes profound alterations in iron metabolism including low efficiency of absorption, high urinary losses and iron depletion (Pérez-Granados *et al.*, 1995).

Information concerning the relationship between type of dietary fat and bioavailability of other elements is very scarce. It seems that palmitic acid acts as a promoter of zinc absorption, arachidonic acid as an inhibitor and caprilic acid does not exert any influence on this metal (Wapnir and Lee, 1990). In general terms, polyunsaturated fats reduce but saturated fats increase zinc retention (Lukaski *et al.*, 1982).

2.2. Interaction used frying oil-minerals:

As indicated above, there is little information on the interrelationship between type of oil and mineral bioavailability, being more rare when it is focused on frying oils. In our laboratory a number of experiments have been performed to study the influence of the consumption of oils from repeated frying of potatoes on the utilization of dietary minerals and some of the results are commented in this review.

A study was undertaken in pregnant rats to examine the influence of consuming unused or used frying olive oil on the absorption and retention of several elements as well as their distribution between maternal tissues and conceptus. Pure olive oil was used in 15 repeated fryings of potatoes without turnover using domestic fryers (Cuesta *et al.*, 1991). Two diets were prepared containing as the only dietary fat 15% of unused olive oil or olive oil from the 15th frying. Pregnant rats were fed these diets during the whole pregnancy and several parameters referring to the mineral status were monitored. Food intake and body weight were similar in the two groups of rats (Navarro *et al.,* 1990). In addition, the nutritive utilization of various minerals did not vary between groups. As an example, in table II several parameters of iron balance during the last week of pregnancy are shown. The amount of iron absorbed and retained was not affected by the dietary fat, although a tendency to increase the urinary losses of this metal was found between days 14 and 18 of pregnancy in the animals that consumed the olive oil from 15 fryings (Pérez-Granados, 1990; Pérez-Granados *et al.*, 1991). Analysis of the products of conception reveiled that there was no change in iron, zinc, calcium and magnesium contents in placentas and foetuses due to the consumption of used frying olive oil (Figure 1). These findings must be related with the low level of alterations in the oil after 15 fryings (Cuesta *et al.*, 1991).

Table II
Iron balance in pregnant rats that consumed unused or used frying olive oil

Days	Group	Ingested (mg/day)	Absorbed (mg/day)	Urinary (μg/day)	Retained (mg/day)	% A/I[1]	% R/A	% R/I
14-18	Olive oil	0.89±0.04	0.39±0.03	13±1	0.38±0.03	43.4±2.1	96.2±0.6	41.9±2.2
	Olive oil 15F[2]	0.88±0.05	0.34±0.04	18±1*	0.32±0.04	37.0±4.0	89.8±4.2	34.8±4.1
18-22	Olive oil	0.70±0.02	0.33±0.03	20±1	0.31±0.03	46.4±3.4	93.8±0.4	43.6±3.3
	Olive oil 15F	0.75±0.04	0.34±0.03	17±1	0.32±0.03	44.4±3.7	94.3±0.9	42.1±3.7

[1] % A/I: Percentage absorbed from ingested; % R/A: Percentage retained from absorbed; % R/I: Percentage retained from ingested.
[2] Olive oil from 15 fryings of potatoes.
Results are means ± SEM of 7-13 animals per group.
* p<0.05 from the corresponding unused olive oil group.

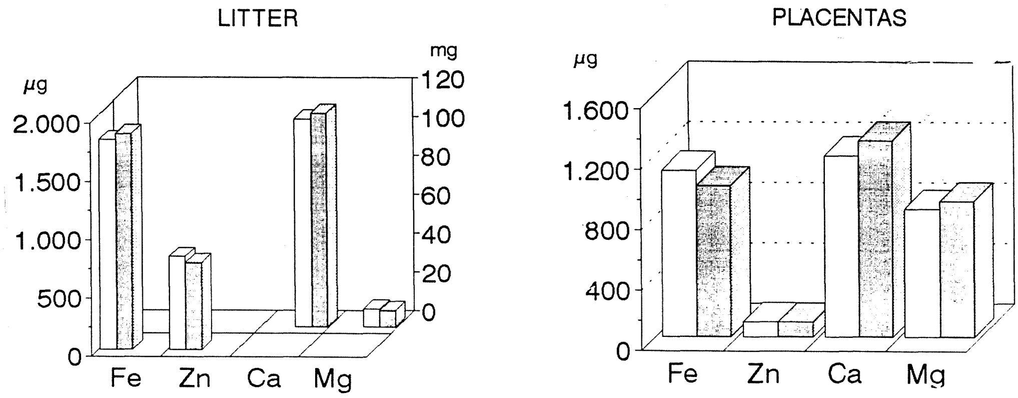

Figure 1
Mineral content on day 21 of pregnancy in litter and placentas of rats fed diets containing unused (open bars) or used (shaded bars) frying olive oil (from Navarro *et al.*, 1990)

Other studies have been carried out under another anabolic condition, that is growth, but in this case oils from a higher number of fryings were used. Olive oil (rich in monounsaturated fatty acids), sunflower oil (rich in polyunsaturated fatty acids) and palm olein (rich in saturated fatty acids) were used in repeated fryings of potatoes, as described previously, up until the oils had 25% of total polar content, the limit of acceptance for human consumption (B.O.E., 1989). This alteration level was reached after 69 fryings with olive oil, 48 fryings with sunflower oil and 80 fryings with palm olein. Olive oil and sunflower oil from frying, both containing 25% of polar compounds, consumed as the only dietary fat (the diet contained 8 % of this fat), produced an elevation in the urinary excretion of zinc compared to unused oils (table III). However, the apparent retention of this element was not significantly reduced, since the urinary excretion represents a small proportion of the absorbed zinc and the values of absorption showed high variations. The mechanisms involved are unknown. Zinc plays an important role in many enzymatic sistems and protects against free radical damage (Wilson, 1989). Since frying produces oxidation of the oil, it is posible that metabolic adjustments occur and zinc is released from tissues being finally excreted in the urine.

Table III
Zinc absorption and retention in rats that consumed unused or used frying oils (μg/day)

Group	Ingested (mg/day)	Absorbed (mg/day)	Urinary (μg/day)	Retained (mg/day)
Olive oil	485 ± 21	136 ± 55	25 ± 3	111 ± 58
Olive oil 69 F[1]	481 ± 24	79 ± 39	30 ± 4	49 ± 43
Sunflower oil	479 ± 24	108 ± 21	23 ± 2	85 ± 23
Sunflower oil 48 F[2]	508 ± 19	111 ± 33	38 ± 4	74 ± 30
ANOVA				
Oil	NS	NS	NS	NS
Frying	NS	NS	P<0.05	NS

[1] Olive oil from 69 fryings of potatoes (total polar content, 25%)
[2] Sunflower oil from 48 fryings of potatoes (total polar content, 25%)
Results are means ± SEM of 10 animals per group.

Other trace elements, iron and copper, appear to be well utilized from diets containing used frying oils with a total polar content of 25 % (unpublished observations).

The bioavailability of a major element, phosphorous, has been described to be rather similar from diets containing olive oil or sunflower oil unused or after being used in frying (Pérez-Granados *et al.*, 1993).

However, magnesium is affected by the presence in the diet of oils used in frying. A common characteristic of olive oil, sunflower oil and palm olein is that after being used in frying they enhance magnesium absorption (Figure 2). The efficiency of absorption was higher with the oils from frying, but in parallel the urinary excretion also increased and consequently the retention of the mineral remained nearly unaffected. It can be hypothesized that the extra amount of magnesium absorbed was not in a molecular form able to be utilized by the body, or the opposite: that the frying process changed the physical and chemical characteriscs of the oils in such a way that magnesium absorption was stimulated and the urinary excretion was also increased to maintain the magnesium balance. The mechanism underlying these phenomenon is unknown. López-Aliaga *et al.,* (1991) reported that medium chain triglycerides enhance the absorption and retention of this mineral probably because these fatty acids do not require bile salts to be absorbed. This suggest that, the products of hydrolytic alteration in the oils may improve the intestinal transport of magnesium.

These findings demostrate that the interaction between dietary fat and minerals varies when the fat comes from a process of frying and that each mineral may have a diferent response.

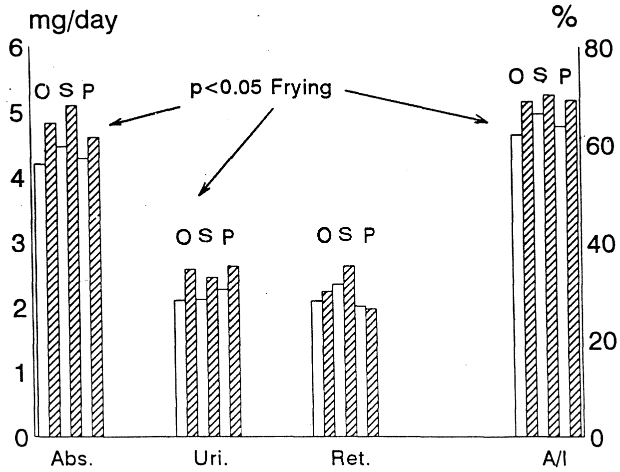

Figure 2
Parameters of magnesium balance in growning rats fed diets containing olive oil (O), sunflower oil (S) or palm olein (P), unused (open bars) or after been used in frying (shaded bars). Abs., absorbed; Uri., urinary; Ret., retained; A/I, percentage absorbed from ingested. Significant differences due to frying are indicated (two ways ANOVA)

3. CONSUMPTION OF FRIED FOODS AND BIOAVAILABILITY OF DIETARY MINERALS

Does the inclusion of fried foods in our diet modify the bioavailability of dietary minerals? This may be an interesting question but difficult to answer, since a variety of factors act together and their combination usually does not produce the same effect as expected according to the behaviour of each factor separately.

As indicated in the first point of this review, frying causes quantitative changes in food composition. However, there are also qualitative changes due to losses of substances and to the exchange that takes place between the frying fat and the food matrix. From a nutritional point of view, the most outstanding ones are those that can take place in the protein or in the fat.

Fish contains proteins with high biological value (Castrillón *et al.*, 1988; Nakajima *et al.*, 1988) and fat with indisputable quality in the prevention of coronary heart diseases (Kromhout, 1993; Turley and Strain, 1993). Whether the alteration of these two nutrients during frying alters the nutritive utilization of minerals is at present under discussion.

Aspe (1992) studied in rats the effects on mineral metabolism of the consumption of diets containing raw sardine, fried sardine (in olive oil), protein from raw sardine or protein from fried sardine. The nutritive utilization of calcium, magnesium and copper was similar in the four cases. However, frying induced a deterioration in zinc utilization, which has mainly been associated with the protein fraction. Under the fried sardine protein regimen elevations in the faecal and urinary excretions of zinc have been reported. Thermal damage of sardine protein during frying includes a decrease in soluble protein, a decrease in sulphur groups, which may be partly caused by the formation of S-S bounds, and losses of cysteine (sulphur amino acid) and histidine. The rest of the amino acids were not reported to vary (Alvarez-Pontes, 1994). Therefore, the changes described by Aspe (1992) related to zinc nutritive utilization and those by Alvarez-Pontes (1994) seem to indicate a cause-effect relationship. It should be pointed out that zinc forms complexes preferably with cysteine and histidine. Both amino acids improve zinc absorption (Sandström and Lönnerdal, 1989) and they are natural ligands of the metal in biological tissues (Bremmer and May, 1989). Particular situations of dietary protein deficit have been demonstrated to produce a state of catabolism and to release zinc which can be excreted in the urine (Varela *et al.*, 1992).

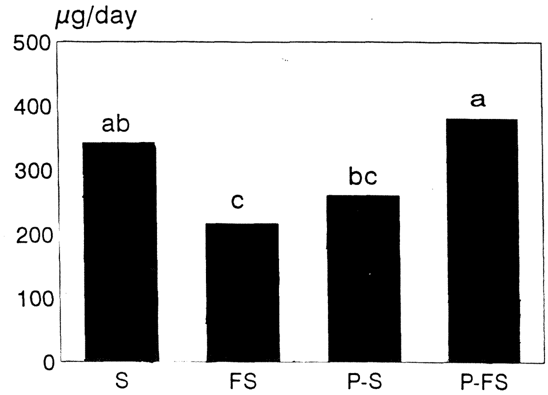

Figure 3
Iron retention in growning rats fed diets containing, as the only dietary protein, raw sardine (S), fried sardine (FS), protein from raw sardine (P-S) or protein from fried sardine (P-FS). Bars not sharing a common letter on the top represent significant differences (p<0.05) (from Aspe, 1992)

In contrast to zinc, the iron absorption and balance has been shown to be more affected by the ingestion of whole fried sardine than the protein from fried sardine (Figure 3). A direct interaction zinc-iron has been proposed (Aspe, 1992). However, in other food systems hydrolysates of proteins have been demonstrated to favor the intestinal transport of iron, as in infant foods for example (Fomon, 1995) and protein degradation products, such as peptones, also enhance the absorption of both haem and non-haem iron compounds (Hazell, 1985).

Table IV
Variations in sardine protein by deep frying

	Soluble protein[1]	– SH[2]	Cystine/ Cysteine[3]	Histidine[3]
Raw sardine protein	80.0 ± 0.5	8.1 ± 0.8	1.33 ± 0.04	4.07 ± 0.11
Fried sardine protein	75.7 ± 0.6*	5.5 ± 0.4*	1.14 ± 0.06*	3.50 ± 0.15*

[1] g/100g of protein; [2] mmol/100g of protein; [3] g/100g of aminoacids
* $p < 0.05$
(From Alvarez-Pontes, 1994)

Fat is the second factor most modified by frying, as previously mentioned, which determines mineral bioavailability. In a controlled study oil from fresh sardines or fried sardines were given to rats as the only dietary fat and compared with olive oil. Food intake and body weight were higher in the group fed the fried sardine oil diet compared with the group fed the olive oil diet and specially low in the group fed with the raw sardine oil diet (Figure 4, Pérez-Granados *et al.*, 1995). Growth retardation in the animals that consumed raw sardine oil was attributed to an excess of n-3 fatty acids and an insuficient provision of n-6 fatty acids. It should be considered that in the case of fried sardine oil, which is a mixture of sardine oil and olive oil used for frying, the supply of n-6 had increased and that of n-3 had decreased being more adequate the n-3/n-6 ratio for the growing rat.

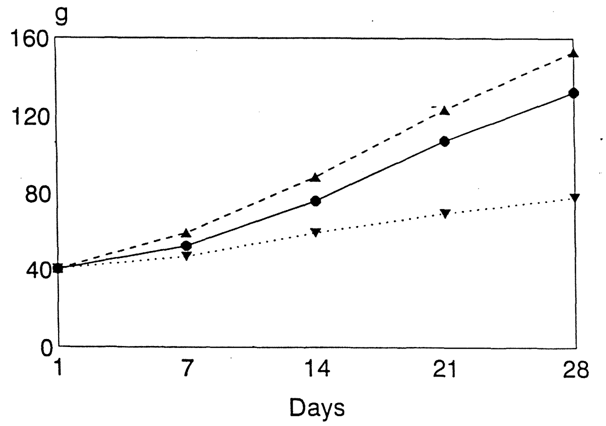

Figure 4
Body weight evolution in rats fed diets containing, as the only dietary fat, olive oil (- -•- -), sardine oil (..▼..) or oil from sardines fried in olive oil (- -▲- -). The differences between the three groups in slopes were significant (p<0.005) (from Pérez-Granados *et al.*, 1995).

The results of iron balance during the fourth week of the assay are shown in Figure 5. Obviously, iron intake reflects the differences in food intake. Faecal iron absorption paralleled its intake, thus no specific adjustment took place at the digestive level in the sardine oil group. In addition, a clear increase in the urinary excretion of iron was observed in this group that caused a lower efficiency of iron retention, parameter of metabolic utilization (%R/A). Consequently, a status of iron deficiency was demonstrated under the sardine oil regimen (table V). These negative influences of the raw sardine oil on iron metabolism were specific, since other trace elements and major elements were not affected (unpublished results) and support the opinion that iron availability from diets rich in saturated fat is higher compared with unsaturated fat (Lukaski *et al.*, 1982; Johnson *et al.*, 1987).

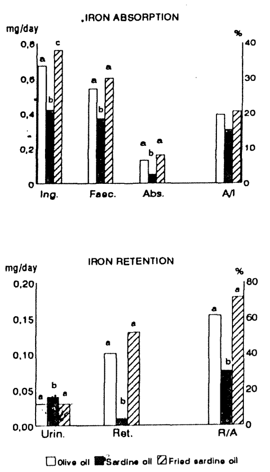

Figure 5
Parameters of iron absorption and retention in rats fed diets containing, as the only dietary fat, olive oil, sardine oil or oil from sardines fried in olive oil. Ing., Ingested; Faec., faecal; Abs., absorbed; A/I, percentage absorbed from ingested; Uri., urinary; Ret., retained; R/A, percentage retained from absorbed (from Pérez-Granados *et al.*, 1995)

Table V

Influence of consuming unused or used frying olive oil on iron balance in pregnant rats

	Olive oil	Sardine oil	Fried sardine oil
TIBC (mg/l)	4.7 ± 0.3 [b]	7.9 ± 0.3 [a]	5.0 ± 0.5 [b]
Hemoglobin (g/100ml)	14.9 ± 0.3 [a]	9.9 ± 1.4 [b]	14.3 ± 0.5 [a]
Liver iron (μg/g)	86.3 ± 8.5 [a]	40.5 ± 2.5 [b]	71.6 ± 8.6 [a]
Spleen Fe (μg/g)	230.4 ± 12.2 [a]	240.0 ± 10.2 [a]	227.8 ± 13.4 [a]
Erythrocytes Fe (μg/g)	902.3 ± 38.4 [a]	819.7 ± 17.8 [b]	864.8 ± 7.7 [a]
Skin Fe (μg/g)	19.4 ± 1.3 [b]	25.5 ± 2.3 [a]	17.1 ± 1.2 [b]

Mean ± SE (n = 5)
Different letters a, b, c indicate significant differences between groups (p < 0.05)
(From Pérez-Granados *et al.*, 1995)

SUMMARY AND CONCLUSIONS

Frying can vary the mineral composition of food due to increasing the mineral concentration caused by dehydration, losses of minerals by leaching into fat medium or losses of minerals due to the increase in cell separation of the cooked tissues. Concerning the influence of frying oils, moderate consumption of olive oil, sunflower oil or palm olein from repeated frying of potatoes without turnover, containing 25% of total polar compounds or less, permits an adequate bioavailability of calcium, magnesium, iron and zinc, with minor variations, as estimated by mineral absorption and retention as well as tissue mineral contents. As regard to fried food, the consumption of sardines fried in olive oil *versus* raw sardines does not seem to affect the availability of dietary minerals. However, the protein from the fried sardines appears to increase faecal and urinary zinc losses. In addition, intake of high doses of oil from raw sardines causes detriment in iron metabolism including iron depletion, but the negative effects disappear with frying in olive oil.

Finally, special attention should be placed on extrapolating data of mineral bioavailability and nutrient interactions based on raw materials because food is not consumed in its raw state and food proccessing plays an important role. Therefore, further investigation on the comparison between culinary methods should be carried out.

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