

Conversion of Ferric to Ferrous Iron in Weight Control Diets

Iron added to canned liquid weight control diets as ferric orthophosphate is largely dissolved and reduced to the ferrous state during 2 to 5 month storage. Since this much time usually elapses between processing and consumption, it appears that all the

flavor and appearance benefits resulting from the fortification with ferric orthophosphate may be enjoyed without sacrificing the nutritional benefits that are attributed to ferrous iron.

During the last 10 yr, a new class of foods designed for weight control has become common. These are formulated foods designed to offer a known limitation of calories and supply protein, vitamins, minerals, and other nutrients in adequate amounts. These foods may be used to replace a single meal but are more useful if consumed as the only food for more extended periods of time in order to control calorie intake. A new food of this class may be referred to as a dietary. While many consider dietary to be a coined word, it is not a new term. The dictionary defines dietary, when used as a noun, as "a regulated allowance of food." This definition describes the products under consideration.

The use of ferric phosphate for the fortification of weight control diets purports to offer certain gustatory advantages not shown by ferrous sulfate. This is especially true in chocolate flavored products. On the other hand, ferrous iron has been claimed to offer some nutritional advantages. Some nutritional text books suggest a preference for ferrous iron and especially condemn ferric phosphate or combinations of ferric iron and phosphate because of the insolubility of this salt. Fritz (1969), as a result of studies with rats and chicks, ranks ferric orthophosphate as a poor source of iron.

Iron metabolism is exceedingly complex, and when one reviews the literature to obtain a more expert view, it is noted that both ferrous and ferric iron have their supporters. While it is often assumed that the iron used in the fortification of food remains in the same state in which it was added, a careful consideration of the problem leads one to doubt this in many cases.

Because many canned liquid diets contain an excess of ascorbate and only a limited amount of headspace oxygen, which is rapidly depleted, it was assumed that iron added as ferrous iron remained in that state. We were not so certain about iron added as ferric phosphate. If the latter iron was eventually in the ferrous state, it would need to be dissolved, ionized, and then reduced. Data will be presented later that suggests solution of the salt is a highly important part of the ultimate conversion.

EXPERIMENTAL

In the course of making some iron determinations by the thiocyanate method of Elvehjem (1930), it was observed that a slight simplification of the method might enable us to estimate both ferrous and ferric iron. The original method calls for drying and ashing the sample, dissolving the ash in hydrochloric acid, converting pyrophosphate to orthophosphate, reacting the ferric iron with potassium thiocyanate, extracting with amyl alcohol, and measuring the red color in the latter medium. A Beckman DB spectrophotometer was used to measure the color at 480 m μ .

The simplification consisted of precipitating the proteins in a 10-ml sample of dietary with 5 ml of concentrated hydrochloric acid, diluting to 50 ml, and filtering with precaution to

prevent oxidation. Ferric iron is determined directly in the filtrate. A 25-ml portion of the filtrate is treated with permanganate to oxidize the ferrous iron to ferric. This solution is diluted to 50 ml and portions used to determine total iron (in the HCl filtrate). Ferrous iron is determined by difference. Traces of protein in the HCl filtrate promote emulsion formation. It is desirable to centrifuge to separate the aqueous and amyl alcohol layers. It may also be necessary to remove the alcohol layer and dry it with a very small amount of anhydrous sodium sulfate before making the spectrophotometric reading. Careful manipulation conserves the 3 ml necessary to fill the Beckman DB cell.

The simplified method was first used on two samples of known total iron content. Sample GJ285AV had been fortified with ferrous sulfate and sample GH265AV had been fortified with ferric phosphate. The results (Table I) indicate that in both cases the iron was in the ferrous state. In each case, most of the iron was in the HCl filtrate.

Our next analysis on sample GA036 suggested the need for further study during storage. Data on this sample indicated that after 2 weeks storage the iron was only about half dissolved, but that the dissolved portion was largely converted to the ferrous state. Sample GA216HN was chosen for the storage study. Total iron was determined in sample GA216HN by the original procedure. This information enabled one to judge when solution and conversion were complete. The data suggested that a major part of the conversion proceeded as quickly as the iron became soluble in the HCl-extractant, but that it took about 2 months for complete solution to occur.

However, more recent data such as that for samples GC-039B6 and GC049DD suggest that solution does not always take place this quickly. Storage temperature may be one factor involved. To date, all data suggest the iron in the diets will be largely converted to the ferrous state by the time the dietary reaches the consumer.

Other methods of iron determination measure iron in the ferrous state. Methods proposed by Kitzes *et al.* (1944) and by Ruegamer *et al.* (1945) employing α, α' bipyridine have been modified and used to verify the observations recorded above. The modification consists essentially of omission of the reducing agent used in the original method to reduce the iron and keep it in the reduced state. With this omission, it becomes highly important to prevent oxidation by keeping liquid surfaces exposed to air at minimum at all times and to complete the analyses as quickly as possible. Even with these precautions it is impossible to say for certain whether the small amount of ferric iron found in the HCl-filtrate exists as such in the dietary or whether it results from oxidation during manipulation of the sample. The results of the direct measurement of ferrous iron are contained in Table I. The results largely confirm the thiocyanate information. Discrepancies may be attributed to the oxidation mentioned above and to other analytical variations.

Ferric orthophosphate is widely used in various types of

Table I. Iron in Liquid Dieteries

Brand	Code	Time stored	Mg Iron in 40 fluid oz				
			Total (ashed sample)	Soluble ^a	Ferric	Ferrous	
						By difference	By α, α' bipyridine
A	GJ285AV ^b	5 mo	16.50	16.07	1.12	14.95	13.12
A	GH265AV	6 mo	16.75	15.84	1.53	14.31	14.66
A	GA036	2 weeks	...	5.67	0.35	5.31	...
A	GA216HN	0	12.02	1.89	0.77	1.12	...
A	GA216HN	1 mo	12.02	6.86	1.00	5.86	6.6
A	GA216HN	2 mo	12.02	11.87	2.36	9.51	...
A	GC039B6	2 mo	14.07	8.32	1.77	6.55	6.38
A	GC049DD	2 mo	10.05	7.04	1.77	5.27	5.20
A	GC059AH	2 mo	16.44	11.35	1.44	9.91	8.28
B	H8271	Unknown ^c	16.93	16.26	1.37	14.89	...
B	H9221	Unknown	20.75	13.50	2.37	11.12	...
B	H9051	Unknown	17.50	14.25	1.25	13.00	...

^a Soluble under conditions of protein precipitation used in analysis. ^b GJ285AV was fortified with ferrous sulfate. Other samples were fortified with ferric orthophosphate. ^c Samples from retail market.

dietaries. For this reason, it seemed appropriate to collect data on a brand B which was competitive to brand A. These are also recorded in Table I. Our observations concerning the conversion apply to both brands, *i.e.*, ferric iron is converted to ferrous iron.

DISCUSSION

If we assume the ferric phosphate is largely suspended rather than dissolved in the dietary at the time of addition, then it appears solution occurs very slowly. After solution, conversion of ferric to the more soluble ferrous iron occurs. The reactions proceed in this direction until all or most of the iron is converted to the ferrous state. This appears to be a most desirable condition, for the iron is reduced, soluble in dilute hydrochloric acid, and presumably readily absorbed for metabolic purposes. Moreover, this permits the use of the ferric phosphate rather than ferrous sulfate, so that the best flavor and color are retained during processing. What flavor

and appearance deterioration, if any, that may occur during the storage conversion of ferric to ferrous iron does not appear to be significant. Ferric orthophosphate fortified dietary has more than 4 yr favorable acceptance by taste panels and consumers. Apparently, the storage changes are minimal.

LITERATURE CITED

- Elvehjem, C. A., *J. Biol. Chem.* **86**, 463 (1930).
 Fritz, J. C., *Fed. Proc.* **28**(692) 2424 (1969).
 Kitzes, G., Elvehjem, C. A., Schuette, H., *J. Biol. Chem.* **155**, 653 (1944).
 Ruegamer, W. R., Michaud, L., Elvehjem, C. A., *J. Biol. Chem.* **158**, 573 (1945).

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