Trace Metals and the Flavor Stability of Margarine[1]

W.G. MERTENS, C.E. SWINDELLS and B.F. TEASDALE,
Research and Development Laboratories, Canada Packers Limited, Toronto, Canada

ABSTRACT

Traces of copper, iron and other metals are present in the oil and the salt used for margarine. The presence of these metals, which act as powerful catalysts for fat oxidation, decreased the flavor stability. Analyses were done by atomic absorption spectroscopy after ashing of 400 g oil and margarine samples. Storage tests are reported with laboratory samples to which different amounts of trace metals had been added, and also with plant production samples. Levels of 0.1 ppm copper led to rapid flavor deterioration. In order to expect good flavor stability, the maximum copper amounts which can be tolerated are about 0.02 ppm. Aside from the importance of having all equipment free of copper, the use of salt low in trace metals or the additions of metal chelating agents are ways to extend the shelf life. The addition of 75-100 ppm EDTA salts as sequestering agents was found to increase the flavor stability of margarine samples significantly.

The flavor stability of margarine depends to a large extent on the conditions (temperature, light) and length of storage, but also on the "built in" stability against oxidation. Trace metals, most of all copper, have long been known to exhibit very strong prooxidant characteristics when present in even small amounts in edible oil products. Bailey (1) stated that "copper, in particular, is a very strong prooxidant, being effective in a concentration of much less than one ppm." Tappel (5) listed copper as "a well known catalyst for the oxidation of unsaturated fats." Cooney et al. (2) stated that "in cottonseed oil both copper and iron were potent oxidative catalysts." A. Vioque et al. (6,7) demetalized olive and soybean oils by passing them through columns packed with cation exchange resins. This lowered the trace-metal content and increased the stability of the oils. "Metal catalyzed lipid oxidation" was the theme of the SIK-Symposium 1967 (3), and many workers (e.g., A. Paton, R. Ohlson) listed the previous work in this field in great detail. Several investigators (e.g., U. Holm) found a direct correlation between the copper content of edible oil products and their stability.

There has always been a strong general interest in determining the amounts of trace metals present, the effects of different amounts and different types of trace metals, and in finding methods which would "neutralize" the strong pro-oxidant effects of these trace metals.

[1]One of 28 papers presented at the Symposium, "Metal-Catalyzed Lipid Oxidation," ISF-AOCS World Congress, Chicago, September 1970.

TABLE I

Deodorized Oil Samples

Sample No.	Trace metals, ppm		
	Cu	Fe	Ni
1-a	0.03	0.25	0.01
1-b	0.03	0.94	0.02
2-a	0.03	0.31	0.06
2-b	0.02	0.56	0.06
3	0.01	0.18	0.20
4	0.01	0.13	0.02
5	0.02	0.16	0.04

When atomic absorption spectroscopy became available as a fast and reliable analytical method for the determination of trace metals in food products like margarine, interest was renewed in these studies related to the flavor stability of margarine.

Several years ago, a project to this effect was started in our laboratories.

TRACE METAL ANALYSES

Trace metal analyses by atomic absorption spectroscopy (AAS) were done on samples of oil, margarine and margarine ingredients. In most cases the samples were analyzed for copper and iron, sometimes also for nickel. It was soon found that the effect of copper is much greater than that of iron or nickel, and the main emphasis was therefore shifted to Cu.

In our method of oil preparation, 400 g of oil are ashed by burning in two 200 g lots in a thoroughly cleaned Vycor-brand evaporating dish. This is then placed in a muffle furnace at 550-600 C for 1-2 hr. After cooling, the residue is dissolved by the addition of 15 ml nitric acid (HNO_3) and 10 ml perchloric acid ($HClO_4$) and careful boiling (covered with watchglass, reflux) for 20 min. The acids are then boiled off until only 1-2 ml is left. After cooling, distilled water is added to make a final volume of 25 ml, thus giving a 16-fold concentration of trace metals (compared to the 400 g oil sample). With this method we expect a total recovery of about 75% of the trace metals originally present in the oil.

The instrument used was a Jarrell-Ash Atomic Absorption Unit, Model 82-350, with a Zeiss total consumption burner using oxygen and acetylene. Determination for copper was carried out at 3247 A, for iron and nickel at 2483 A. Hollow cathode lamps were used with multipass optics (three passes).

The following results were obtained with deodorized oil samples (Table I), margarine samples (Table II), water (Table III), and salt samples (Table IV). The sample numbers designate different refineries from our own and other companies.

In the oil samples, copper levels were below 0.03 ppm, iron levels below 1 ppm and nickel levels below 0.2 ppm.

TABLE II

Margarine Samples

Sample No.	Trace metals, ppm	
	Cu	Fe
1-a	0.03	0.36
1-b	0.03	0.28
1-c	0.03	0.92
2-a	0.03	0.35
2-b	0.06	0.60
3-a	0.02	0.55
3-b	0.05	0.21
3-c	0.04	1.35
3-d	0.03	0.80
3-e	0.11	1.20
1-d	0.07	0.70
1-e	0.07	0.60
1-f	0.004	0.07
4	0.07	1.0
5-a	0.08	—
5-b	0.02	0.47
6	0.06	0.62
7	0.03	0.27

TABLE III

Water Analyses

Sample No.	Trace metals, ppm Cu	Fe
1	Nil	0.2
2	Nil	Nil

In margarine samples, copper levels were generally between 0.02 and 0.07 ppm and iron levels generally between 0.3 and 1 ppm.

Water analyses gave very low levels of copper and iron. In Table IV our own results are compared with the figures taken from the manufacturer's specification sheets. It should be mentioned that Canadian margarine contains about 3% salt, and this would, at high copper levels, contribute a significant amount of this metal to a finished margarine. It is interesting to note that varieties of highly purified salt are now commercially available; their manufacturing process includes a "metal chelating" step.

TABLE IV

Salt Samples

Salt samples	Trace metals, ppm Cu	Fe
Laboratory results		
Windsor Hi-Grade	0.10	
Windsor 999	0.12	
Windsor Hi-Grade 999	0.04	
Manufacturers specifications		
Windsor Hi-Grade	0.5	1.0
Windsor 999	0.4	0.5
Windsor Hi-Grade 999	0.1	0.4

FLAVOR EFFECTS OF TRACE METALS, WITH AND WITHOUT EDTA SALTS

Laboratory Tests

Tests have been made in an attempt to produce the typical, bitter, metallic off-flavors by the addition of trace metals to laboratory margarine samples. Regular margarine ingredients were obtained from the plant.

1. Oil phase contained emulsifiers, color, and vitamins.
2. Water phase (the margarine "milk") contained salt. After heating the oil to 130 F, the two phases were mixed in a Waring blender, and the margarine was then solidified on a cake pan previously placed on dry ice. The margarine samples were stored at 45 F in a covered beaker.

Test Series 1. Margarine samples were prepared according to the above procedure, but with the addition of copper and iron salts to the oil, or water phases, or both, prior to blending. Copper and iron were added as stearate to the oil phase, and to the water phase as Cu $(NO_3)_2 \cdot 3H_2O$ and Fe $Cl_3 \cdot 6H_2O$. The concentration was in all cases 10 ppm of iron or copper in the margarine. The results are listed in Table V.

Copper either in the oil or water phase gave a strong, bitter and metallic flavor. Initially, and even after 12 days of storage, iron alone did not affect the flavor significantly.

Test Series 2. In test series 2, margarine samples were prepared according to the procedure outlined above but varying amounts of copper stearate were added to the oil. The disodium salt of ethylene diamine tetraacetic acid (Na_2EDTA) was added as a metal scavenger to the water phase of several samples. The samples were stored at 45 F and tasted after two and nine days.

The use of ethylenediamine tetraacetic acid (EDTA), in particular the disodium or the calcium disodium EDTA, as a chelating agent in food products has been known for some time, and is permitted by the Canadian Food and Drug Regulations for certain foods. It is probably the most widely known, most widely used, and one of the most effective chelating agents for copper.

Melnick (4) listed test work with margarine samples to which citric acid or mono-isopropyl citrate in a mono- and diglyceride vehicle and salts of EDTA (disodium or calcium disodium EDTA) had been added. In all cases where EDTA had been used, the flavor stability of the margarine samples was improved over that of the control samples.

Table VI gives the test results; the additives are always given as ppm for the whole margarine formulation.

The results show that very small amounts of copper can lead to an immediate development of metallic, bitter flavors. Without EDTA all samples with more than 0.1 ppm copper were rated as poor, but when EDTA was used as metal scavenger, copper amounts could be increased to 1 ppm to give comparable results.

In another test series, different chelating agents were evaluated with laboratory-prepared margarine samples. Copper nitrate $Cu(NO_3)_2 \cdot 3H_2O$ was added to the water phase just prior to use, in an amount to supply 0.04 ppm of copper to the finished margarine. This was done to obtain a uniform copper level of about 0.05-0.06 ppm in the finished samples (which was confirmed by AAS).

The following additives were used: control, no added chelating agents; monoglyceride citrate (MGC) (0.01%); disodium salt of ethylene diamine tetraacetic acid (EDTA) (0.01%); a combination of MGC (0.01%) and EDTA (0.01%); sodium hexametaphosphate (0.1%); sodium tripolyphosphate (0.1%); and sodium pyrophosphate, tetra (0.1%).

In all the above samples, except for MGC, the chelating agents were added to the water phase prior to blending; the percentages indicate the level in the finished margarine. For MGC, addition was to the oil phase and the percentage level applies to the oil phase. The margarines were then stored at 45 F for at least 24 hr before tasting.

It was found that the samples containing 0.01% diso-

TABLE V

Laboratory Margarine Samples With Metal Salts

Sample No.	Oil phase Fe	Cu	Water phase Fe	Cu	Flavor comments at 12 days storage
2	No additives				Fair, average
3	x				Fair
4		x			Poor, metallic, bitter
5	x	x			Poor, metallic, bitter
6			x		Fair
7				x	Poor, metallic, bitter
8			x	x	Very poor
9	x		x		Fair
10		x		x	Very poor
11	x	x	x	x	Very poor

TABLE VI

Laboratory Margarine Samples

Sample No.	Addition to oil phase, ppm Cu	Addition to water phase, ppm Na_2 EDTA	Flavor comments	
			2 Days storage	9 Days storage
14	3	—	Very poor	Very poor, bitter, metallic
15	1	—	Very poor	Very poor, bitter, metallic
16	0.3	—	Poor	Very poor, bitter, metallic
17	0.1	—	Metallic, medium	Old, slightly metallic
18	0.03	—	Strong, fair	Fair
19	3	100	Poor	Very poor, bitter, metallic
20	1	100	Fair	Old, slightly metallic
21	0.3	100	Fair	Old, slightly metallic
22	0.1	100	Fair	Fair
23	0.03	100	Good	Fair
24	—	100	Good	Satisfactory
25	—	—	Good	Satisfactory

dium EDTA had good flavors after two weeks of storage at 45 F, whereas the control sample had a strong, poor, bitter metallic flavor after only three days of storage. A combination of MGC and EDTA gave similar flavor results as when EDTA was used alone; however this margarine did contain milk which in itself provides an edible citric acid component.

Under the conditions of these tests the flavor of margarine containing only MGC was not better than the flavor of the control sample.

Of the three phosphates tried in these tests, the only one which showed any promise was sodium hexametaphosphate, but even when this was used the margarine had a very slight metallic flavor, which was absent in all samples containing EDTA.

Bacterial growth was noted in the samples containing phosphates after a relatively short storage time; in contrast, the samples with EDTA showed no bacterial spoilage even after a relatively long storage time.

Plant Tests

Two plant tests were conducted. In each case one small churn was run without EDTA as control, and an equal churn from the same oil batch with EDTA. Disodium EDTA (0.01% of the weight of the finished margarine) was dissolved in the water phase (margarine milk) as the last ingredient, that is after the addition and dissolution of the salt.

Margarine prints were stored at 45 F and tested organoleptically. The samples with EDTA had a substantially better flavor stability that the control samples without EDTA.

Numerous later plant tests with disodium EDTA and calcium disodium EDTA at levels of between 50 and 100 ppm confirmed the earlier test results of improved flavor stabilities.

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