Trace Metal Contents, Chemical Properties and Oxidative Stability of Capelin and Herring Oils Produced in Norwegian Plants

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ABSTRACT

The iron and copper contents of 14 crude capelin oils, two herring oils and one blend produced in oil meal plants in northern Norway were determined by atomic absorption spectroscopy (AAS). Their oxidative stability, peroxide (PV), benzidine (BV) and iodine values (IV), free fatty acids (FFA) and tocopherol contents were also evaluated. The oxidative stability was found to be more dependent on the tocopherol content and BV of the crude oils than on their content of trace metals. Changes in iron, copper and nickel contents were determined by AAS after refining and hydrogenation of marine oils in two Norwegian hydrogenation plants. The content of trace metals in the oils and hydrogenated products decreased as a result of alkali refining and bleaching to the lower limits of detectability by the method used, and amounted to 0.01 (oils), 0.02 and <0.3 ppm for iron, copper and nickel respectively.

INTRODUCTION

In 1955, Walsh (1) introduced the atomic absorption spectrophotometry (AAS) technique. The analytical applications of the outlined method have grown very rapidly as it provided a needed accurate means for the quantitative determination of trace metals in various products. The catalytic effect of certain trace metals in the mechanism of fat oxidation is well known (2,3). The determination of trace metals by AAS in oils and fats may therefore be of importance to establish their original concentrations and to detect changes in metal contents as a result of contamination and industrial processing.

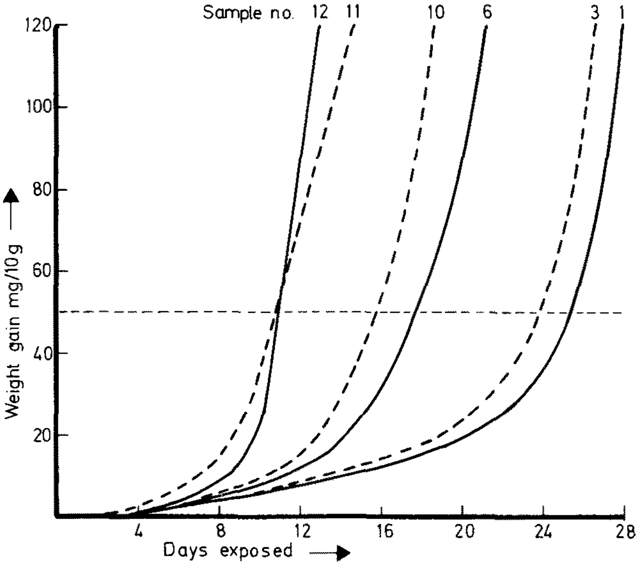

FIG. 1. Oxidative stability curves for capelin oil samples.

In the present investigation the iron and copper contents in capelin and herring oils were determined and corrleated with other properties. In addition the change of trace metal contents was determined by AAS in samples from various industrial processing steps used for production of edible hydrogenated herring oil.

MATERIALS AND METHODS

Samples of capelin and herring oils were supplied by various processing plants on the coast of northern Norway and stored in brown bottles. Capelin are difficult to process immediately after they are caught and must autolyze to some extent before the oil can be satisfactorily pressed out. They are therefore stored at least one or two weeks at about 0-10 C before processing, and free fatty acids (FFA) in the oil usually amount to 2-5% or more. Oil and fat samples from the refining and hydrogenation process were supplied by hydrogenation plants in southern Norway.

Determination of Trace Metals by Atomic Absorption Spectroscopy

The procedure outlined by (4) was followed for the

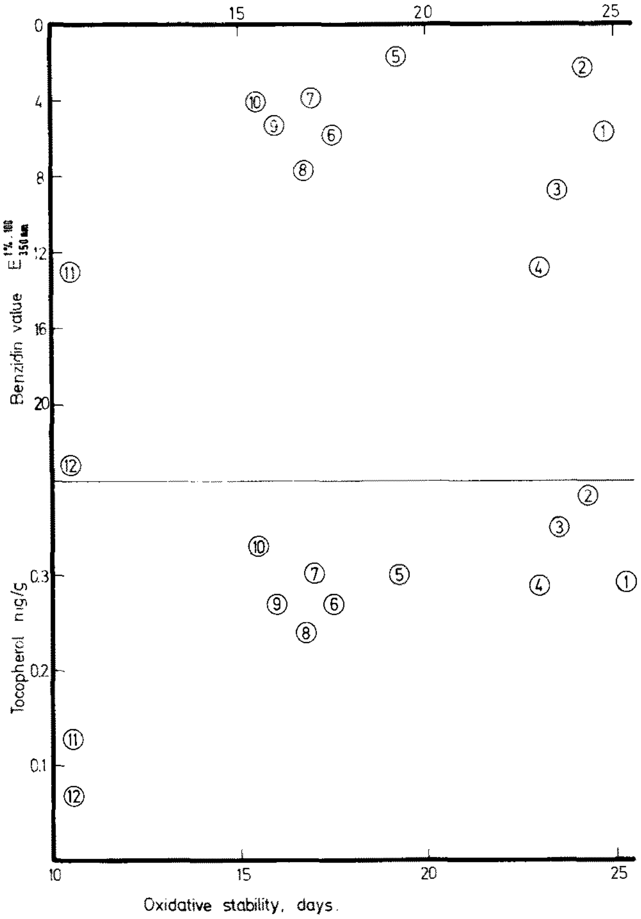

FIG. 2. Oxidative stabilities of crude capelin oils versus their tocopherol contents and benzidine values. Numbers in rings (points) indicate sample number (Table I).

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TABLE I

Iron and Copper Content and Chemical Properties of Crude Capelin and Herring Oils From Various Oil and Meal Producing Plants

Oil sample number	Plant number	Oil	Iodine value (Wijs), g I/100g	Free fatty acids, % as oleic	Peroxide value, mc/kg	Benzidine value, $E^{1\%}_{350\,nm}\cdot 100$	Oxidative stability, days[a]	Iron ppm[b]	Copper ppm[b]	Tocopherol, mg/g	Color
1	5	Capelin	102.0	2.35	1.0	4.9	25.25	0.07	0.03	0.29	Turbid Yellow
2	4	↓	99.5	6.9	1.4	2.35	24.25	0.85	0.06	0.38	Yellow
3	1[c]		95.0	5.4	1.3	8.8	23.5	4.6	0.12	0.35	Yellow
4	1[c]		100.0	4.5	5.8	13.0	23.0	4.8	0.15	0.29	Yellow
5	3		100.3	17.4	1.3	1.7	19.25	10.06	0.21	0.30	Dark brown
6	3		102.75	16.2	0.75	5.7	17.5	3.95	0.40	0.27	Dark brown
7	3		102.5	5.05	11.7	3.7	17.0	0.52	0.06	0.30	Orange
8	2[c]		102.5	5.5	1.4	7.6	16.75	1.66	0.09	0.24	Yellow
9	3		101.0	13.0	5.3	5.3	16.0	1.64	0.27	0.27	Dark brown
10	3		100.0	4.55	7.3	4.1	15.5	1.33	0.06	0.33	Yellow
11	3		94.5	7.0	5.8	13.0	11.0	1.93	0.11	0.13	Yellow
12	1		101.5	3.9	7.0	23.3	11.0	1.38	0.24	0.07	Yellow
13	4	Capelin[d]	101.0	8.5	0.4	5.1	9.5	0.44	0.06	0.44	Yellow
14	3	Capelin[d]	105.0	5.15	23.5	10.5	15.75	0.07	0.09	0.33	Orange
15	2	Blend[e]	112.5	8.45	2.8	9.5	5.5	10.8	0.73	0.20	Brown
16	1	Herring	129.0	6.4	7.8	29.6	4.0	10.2	0.12	0.21	Brown
17	1	Herring	141.5	4.2	4.4	6.25	10.5	0.5	0.08	0.13	Red

[a] Days at 25 C to reach 50 mg weight gain/10 g.

[b] Scale expansions 2 and 5 were used for Fe and Cu respectively.

[c] Dried capelin meals from plants 1 and 2 were found to contain 256 and 192 ppm Fe and 4.9 and 4.3 ppm Cu respectively. Sale expansions 1 and 2.

[d] Oil produced from stick water concentrate corresponding to oil samples 2 and 7 respectively.

[e] Capelin and herring oils blend (1:1).

TABLE II

Changes in Peroxide and Benzidine Values of
Eight Capelin Oil Samples After Autoxidation for 26 Days at 25 C

Oil sample number	Processing plant	Iron, ppm	Copper, ppm	Peroxide value Original	Peroxide value After oxidation	Benzidine value Original	Benzidine value After oxidation	Oxidative stability days[a]
5	3	10.06	0.21	1.3	540	1.68	465	19.25
6	3	3.95	0.4	0.74	665	5.65	455	17.5
7	3	0.52	0.06	11.7	735	3.66	460	17.0
8	2	1.66	0.09	1.4	670	7.57	620	16.75
9	3	1.64	0.27	5.3	775	5.28	662	16.0
10	3	1.33	0.06	7.3	940	4.1	880	15.5
13[b]	4	0.44	0.06	0.42	540	5.06	386	9.5
14[b]	3	0.07	0.09	23.55	830	10.5	565	15.75

[a] See Table I for explanation.

[b] Oils from stick water concentrate.

determination of iron, copper and nickel in the examined marine oils. Perkin-Elmer model 303 apparatus with scale expansion facilities and Boling head was used. Instrumental operating conditions and settings were conducted according to specifications outlined in (5). Scale expansion employed in each case was indicated.

The oil samples were examined in a 20% (v/v) solution of ethyl acetate. With hydrogenated fat samples a 10% solution was used. In one case methylisobutylketone (MIBK) was used to dissolve samples obtained from two hydrogenation plants for iron determination. The sensitivity (5) for iron determination by AAS increased when ethyl acetate was used instead of MIBK. The increased sensitivity varied with different aspiration rates. It was, however, considerable in every case and a factor of 1.6 was noted. Through all AAS analysis good sensitivity was achieved with ethyl acetate. The sensitivity amounted to 0.02 ppm or better for copper, 0.05 ppm for nickel and 0.04-0.05 ppm for iron, per cent absorption, which could be read with an accuracy of ca. ±0.1 per cent.

For each prepared group of oil solutions for AAS analysis a standard curve was established. Standard solutions having known concentrations of the corresponding metal salt of 2,4-pentadione (J.T. Baker Chemical Co.) were made with ethyl acetate containing 20% refined, bleached and deodorized peanut oil. The standard and unknown oil solutions were run in succession in the AAS apparatus. A blank solution of ethyl acetate containing 20% peanut oil was used for the zero setting. The standard curve was made by plotting the averaged absorbance readings for the standards against concentration. Trace metals contents were calculated on a w/w basis.

Chemical Examinations of the Oils

The following constants: iodine value (IV), percentage free fatty acids (FFA) and peroxide value (PV) of the examined oils were determined essentially according to methods of the American Oil Chemists' Society (6). Benzidine value (BV) which measures the α-β unsaturated aldehydes in fats was determined as described by Holm et al. (7) with modifications recommended by G. Wode (personal communication). The BV ($D^{1\%\cdot 100}_{350\,nm}$) was determined by reacting benzidine with the fat (0.5-1.0 g) in absolute alcohol-hexane (1:2) solution. The resultant yellow color was measured at 350 nm.

Total tocopherol contents were determined by the Emmerie-Engel procedure (8). Determinations were made after saponification under nitrogen and in the presence of pyrogallol. The washed unsaponifiable matter was dissolved in heptane, $FeCl_3$ + α,α'-dipyridyl solutions added, and the absorption was measured at 520 nm after 3 min.

Oxidative stability was measured by weight gain of oil kept in air. Ten-gram samples were accurately weighed in petridishes (9 cm diam.) and placed overnight at 50 C in a

TABLE III

Effect of Refining, Bleaching, Deodorization and
Hydrogenation on Trace Metals Content in Oils and Hydrogenated Fats

Sample	Iron,[a] ppm	Copper, ppm	Nickel, ppm
Hydrogenation plant 1:			
Crude herring oil	9.5	0.1	<0.3
Alkali refined herring oil (1106)	0.23	0.05	---[b]
Alk.ref., bleached herring oil (1106)	~0.01	~0.02	---
Hydrogenated herring oil (1106)	<0.04	0.05	8.7
Hydrogen., alk.ref. herring oil (1106)	<0.04	0.03	1.7
Hydrogen., alk.ref., bl. marine oil (1107)	<0.04	<0.02	<0.3
Hydrogen., alk.ref., bl., deodorized marine oil (1107)	<0.04	~0.02	<0.3
Hydrogenation plant 2:			
Crude herring oil	2.3	0.06	<0.3
Alk.ref. herring oil (washed, dried)	0.02	0.04	---
Alk.ref., bl. herring oil (autoclave)	0.03	-----	---
Alk.ref., bl. herring oil (filter press)	~0.01	0.04	---
Hydrogen. herring oil	< 0.04	0.13	3.9
Hydrogen alk.ref. herring oil	< 0.04	0.06	<0.3
Hydrogen., alk.ref., bl., deod. herring oil	< 0.04	<0.02	<0.3

[a] Oil samples were dissolved in methylisobutylketone in case of Fe and in ethyl acetate for Cu and Ni analysis. Scale expansion 2 was used for Fe; the aspiration rate and the velocity of acetylene supply was adjusted to give maximum sensitivity which amounted to ca. 0.06 ppm/% absorption. Scale expansions 2 and 5 were used for Ni and Cu respectively.

[b] Undetermined.

vacuum oven (20 mm Hg) to remove traces of water. After cooling in a desiccator the samples were reweighed and placed in air under glass basins at 25 C and weighed twice weekly. Weight gains were calculated for 10 g dried oil and curves for progressive weight gain versus keeping time were drawn (Fig. 1). The time required for 50 mg increase/10 g oil was taken as index for stability.

Iron and Copper in Capelin Meals

Meals from plants 1 and 2 were dried for 2 hr at 105 C and 10 g samples were ashed in a muffle furnace for 6 hr at 550 C. The ash was dissolved in 9% hydrochloric acid (Merck), transferred quantitatively into a 100 ml volumetric flask and diluted to the mark with deionized water. The solution was analyzed for iron and copper by AAS. Corresponding aqueous standard solutions were run in succession along with unknown solutions, and the iron and copper contents of the acid solution used to dissolve the ash were determined.

RESULTS AND DISCUSSION

Capelin and Herring Oils

The data shown in Table I indicate the properties as well as several relationships between the values of the capelin oils. Some correlation is noted between FFA and iron. Oils with the lowest iron content correspond mainly to the lowest FFA values. The oxidative stabilities of the capelin oils show no correlation with the content of iron, but some tendency to correlation with that of copper. The influence of per cent FFA is negligible. To an extent, a correlation exists between PV and the oxidative stability, but is more pronounced for BV. The tocopherol values for the capelin oils show the best correlation with stability (Fig. 2). The mean tocopherol value for the four oils possessing the best oxidative stability–23-25 days–was ca. 0.33 mg/g, and for the two with the lowest oxidative stability–11 days–0.10 mg/g. The mean values for PV, BV and copper for these groups, 2.4-6.4, 7.3-18.1 and 0.09-0.18 respectively, indicate some correlations also, whereas the corresponding iron contents are 2.6 and 1.65. For the stability between 16 and 18 days, the tocopherol content varied between 0.24 and 0.33 mg/g, the BV from 1.7 to 7.6. Such variations might be due to differences in raw material or processing conditions, which might have influenced the content of other natural antioxygenic compounds, e.g., phospholipids. The variations for the PV and copper contents are much greater for this stability group. (After this manuscript had been accepted for publication the authors became aware of an article in *Commercial Fisheries Revue,* [May 1957–Supplement] by E. Einset, H.S. Olcott and M.E. Stansby: "Oxidative Deterioration in Fish and Fishery Products. Part IV: Progress on Studies Concerning Oxidation of Extracted Oils," regarding determination of the oxidative stability and tocopherol content of 10 different fish oils and one whale oil. The tocopherol content varied from 0.04-0.63 mg/g oil, and they conclude: "The induction period of the oils tested was roughly proportional to the tocopherol content and roughly inversely proportional to the iodine number." The above results for capelin and herring oils are in good agreement with this conclusion.)

The oils produced from stick water concentrates, samples 13 and 14, contained less iron and about the same amount of copper as the corresponding oils, samples 2 and 7, extracted before the concentration (in stainless steel evaporators), but sample 13 showed a much lower stability than did sample 2 (Table I).

In conclusion, the iron or copper content of the crude capelin oils has no or very little direct correlation with their oxidative stability. Similar observations were reported by Pokorny (9). Therefore trace metals from the processing equipment do not seem to be decisive factors for the stability against oxidative deterioration of capelin oils in the crude state.

The capelin meals contained ca. 50-100 times as much iron and ca. 40-50 times as much copper as the corresponding oils (fn.[c] Table I).

Capelin meal oils extracted with pentane-hexane from six dried press cakes and meals protected against air in tight containers, from plants 1 and 2, were found to contain 1.5-21.8 ppm iron and 1.3-3.9 ppm copper. Their iodine values (10) were 144-168 and FFA contents 13.2-35.2 per cent.

The higher IV of the herring oils as compared to capelin oils may account for the remarkably lower oxidative stability of the former (Table I). The difference in stability time of samples 16 and 17 might be due to the much higher BV of sample 16. The fairly low oxidative stability of sample 15 may be explained by its extraordinarily high copper content. A herring oil prepared in glass apparatus in the laboratory was found to contain 0.42% FFA, <0.01 ppm iron and 0.08 ppm copper.

The BV and PV of eight capelin oils were determined after measuring their oxidative stability (Table II). No direct correlation was observed between PV or BV after autoxidation for 26 days and their corresponding initial values or initial trace metal contents.

Effect of Alkali Refining, Bleaching, Deodorization and Hydrogenation on Trace Metals Content

The data in Table III present changes in iron, copper and nickel content of herring oils during processing in two hydrogenation plants. In both cases the alkali refining substantially decreased the iron content, which was further reduced by bleaching, and the finished hydrogenated product was very low in iron as determined by AAS analysis. The copper content in the crude herring oils was fairly low and decreased further to a negligible quantity (0.02 ppm or less) after refining. As a result of hydrogenation nickel and some copper were introduced in the oils; however, the ordinary post-refining and bleaching treatments sharply decrease the nickel and copper content to less than 0.3 and 0.02 ppm respectively. These values are in good agreement with result obtained by neutron activation analysis for corresponding samples reported by plant 1, and clearly indicates the low level of trace metals in edible hydrogenated herring oil. Accordingly, one might regard the published relatively high concentration of iron (3.4-4.2 ppm) and copper (0.4-1.1 ppm) obtained by AAS analysis in hydrogenated herring, whale and rapeseed oils by Slavin (11) with some reservation.

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I. Gukild performed the AAS determinations and S.Øyasaeter and K. Frog performed the spectrophotometric determinations of BV and tocopherol.

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