The Analysis of Organically Bound Elements (As, Se, Br) and Phosphorus in Raw, Refined, Bleached and Hydrogenated Marine Oils Produced from Fish of Different Quality[1]

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ABSTRACT

Marine oils have been produced in pilot plant by boiling, pressing and separation of the press liquor from raw material (mackerel and herring) of different levels of spoilage. The difference in quality is obtained by varying the period of storage. Some of the oil samples have been refined and hydrogenated. In samples taken both from the raw oils and from oils at the different steps in the processing, organic bound arsenic, selenium, bromine and phosphorus are analyzed. When the raw material deteriorates during storage, an increase in the selenium and phosphorus content in the oils produced from these materials is observed, whereas the bromine and the arsenic content is nearly constant. During the refining the arsenic and phosphorus disappear almost completely from the oils, whereas the selenium content is reduced to about two-thirds and the bromine content is nearly unaffected. In the hydrogenation step the selenium disappears relatively fast and the bromine more slowly.

INTRODUCTION

It is well known that, in catalytic hydrogenation of oils, the marine oils will cause a considerably faster inactivation of the catalyst than the oils of vegetable origin. Sulphur compounds are the most frequently occurring of these catalyst contaminants (1,2). However it is possible that other compounds present in marine oils could affect the catalyst. Bromine, arsenic and selenium, which are all present in the form of fat soluble compounds in these oils, can here be mentioned as potential contaminants. It has furthermore been observed that the poisoning of the catalyst in hydrogenation of marine oils becomes more pronounced as the quality of the raw material from which

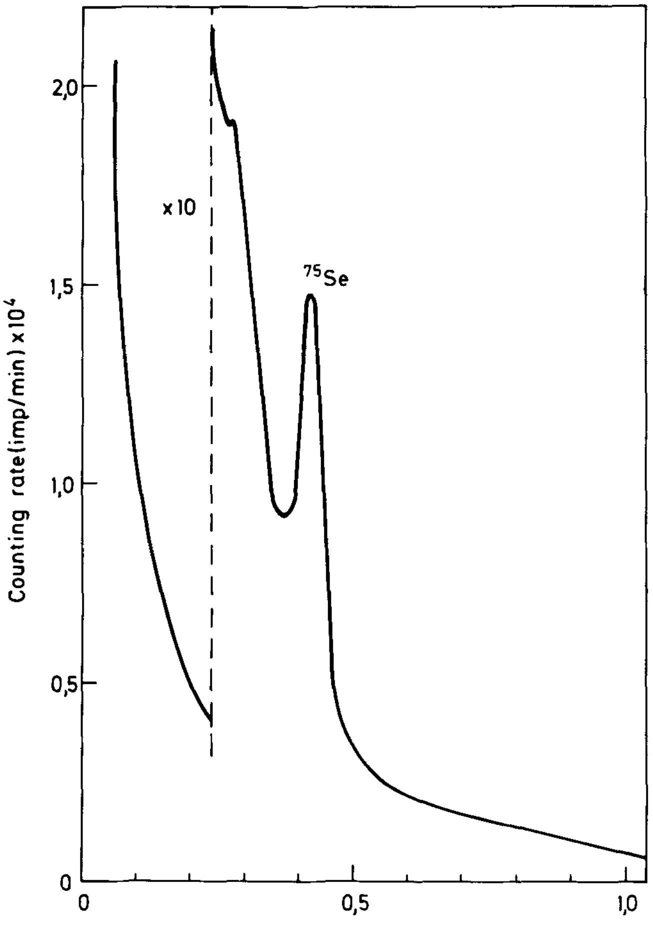

FIG. 1. γ Spectrum of neutron-activated crude oil sample registered 1.5 months after inactivation, showing the bremsstrahlung spectrum from ^{32}P and the sum peak of ^{75}Se at 0.4 MeV.

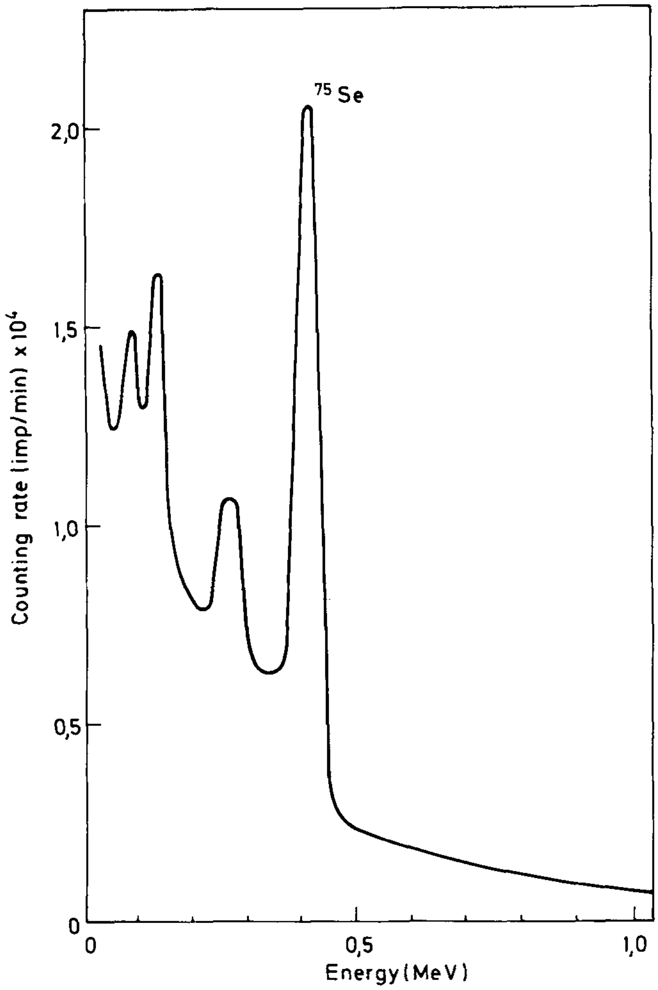

FIG. 2. γ Spectrum of a neutron-activated bleached oil sample registered 1.5 months after activation. Only the γ spectrum of ^{75}Se can now be seen.

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[1] Presented at the ISF XIth World Congress, Gøteborg, Sweden, June 1972.

TABLE I

Trace Elements in Oil Produced from Fish of Different Quality

Sample	Locality and date of catch	Storage, days	TVN,[a] mg N/100 g	FFA in the oil, %	Se, ppm	Br, ppm	P, ppm	As, ppm
Herring	West coast of Norway 6/2/70	0	13	0.6	0.09	4.3	<1	6.5
		6	88	2.3	0.14	4.0	72	6.6
		13	156	6.7	0.28	4.1	66	7.6
Herring	Shetland 13/10/70	0	13	0.2	0.02	4.4	6	5.3
		2	22	0.6	0.04	5.0	12	5.4
		5	83	9.8	0.22	4.3	111	5.3
		8	133	16.4	0.26	3.8	230	5.3
Mackerel	North Sea 24/10/70	0	6	0.2	0.05	3.1	<2	5.2
		3	35	1.3	0.06	2.5	8	5.2
		7	91	11.5	0.11	3.3	99	5.2
		10	134	16.5	0.11	2.9	106	4.9
Mackerel	West coast of Norway 8/9/70	0	18	0.3	0.05	3.7	8	4.6
		6	87	1.9	0.19	3.7	12	5.5
		12	141	3.8	0.21	3.2	20	4.9
Capelin	North coast of Norway	0	31	2.5	0.09	3.6	4	9.1
		---[b]	116	10.4	0.12	3.4	141	7.8
		---[b]	198	10.9	0.10	3.6	137	8.5

[a] TVN = Total volatile nitrogen; FFA = free fatty acids.

[b] Low quality raw material.

the oils is produced decreases. This effect can be correlated with an increase of the sulphur content in the oil (2).

The presence of selenium-containing compounds in marine oils was demonstrated in our laboratory 1-2 years ago (3). No information exists to indicate whether the content of these compounds increases as the raw material deteriorates. Concerning the bromine, it has been shown that bromine-containing compounds are present as both neutral and polar lipid soluble compounds, and it is suggested that the bromine seems not to be associated to one or more specific groups of lipids (4). It is therefore less probable that the bromine content of the oil will be affected by the quality of the raw material from which the oil is produced.

The variation of the content of arsenic in oils produced from raw material in which the quality ranges from good to very bad is not known. However it has previously been shown that most of the arsenic is removed during the alkaline-refining process (5) and will probably not have any inactivating effect on the catalyst.

The purpose of this investigation was in the first instance to study in more detail how the selenium, arsenic, phosphorus, i.e., the phospholipids, and the bromine contents varied in oils produced from raw fish materials of differing qualities, and thereafter to follow these elements in the oils during the alkaline-refining, the bleaching and the hydrogenation processes.

Neutron activation was used as an analytical method for determining the elements to be analyzed. Even though the precision of this method is not as great as other methods based on spectrophotometry for phosphorus per se, it is quite adequate for the large changes measured in the present work. Furthermore it is advantageous to be able to measure phosphorus along with selenium, arsenic and bromine on the same samples, especially when the determination is performed nondestructively.

EXPERIMENTAL PROCEDURES

Herring and mackerel were used in these experiments. In addition some industrially produced capelin oils of varying quality were analyzed. The oils were produced from raw materials which had been stored for varying lengths of time. The intervals at which samples were taken from storage were chosen so that the quality of the fish changed from good to very bad. The storage took place under anaerobic conditions, and the temperature was kept at a level corresponding to air temperature normally encountered during corresponding industrial storage. The storage period varied from 0-13 days. The condition of the fish material was characterized by analyzing the total volatile nitrogen (TVN) content in the raw material, and the free fatty acid (FFA) content in the oils produced. (TVN and FFA were determined at the Norwegian Herring Oil and Meal Industry Research Institute.) A few chosen series of oils were then alkaline-refined, bleached and hydrogenated. The hydrogenation was carried out under standard conditions in a laboratory scale using nickel catalyst (3). Oil samples were taken at given intervals. Further information concerning the treatment and the characterization of the oils are given elsewhere (3).

Neutron activation was used for the analysis of bromine, selenium, arsenic and phosphorus. Only a brief description of the analtyical technique is given here. Samples of ca. 0.5 g were weighed and sealed into quartz ampoules. The samples, together with bromine, selenium, arsenic and phosphorus standards, were irradiated with thermal neutrons at a flux of ca. 5 x 10^{12} n/cm^2 sec for 20 hr in the nuclear reactor JEEP 2 at Kjeller, Norway. When the irradiation process was completed, the oils were transferred to inactive glass vials, and their activities counted on a 400 channel γ spectrometer with a 3 x 3 in. NaI well-type crystal. The induced activity in bromine (^{82}Br) and in arsenic (^{76}As) with half lives of ca. 34 hr and 26 hr, respectively, can be measured 1-7 days after irradiation. The radioactive sodium isotope ^{24}Na was detected in some of the samples, and in these cases the counting of the bromine and the arsenic activity was postponed until the interference from ^{24}Na compton became negligible.

When the radioactive bromine and arsenic isotopes in the oils had disintegrated, the radioactive selenium isotope ^{75}Se with a half life of 120 days could be registered. The neutron activated phosphorus, ^{32}P emits only β rays when decaying and can be determined by measuring the "bremsstrahlung." After subtracting the background activity and the contributions from the other radioactive isotopes, in particular ^{75}Se, the phosphorus was analyzed by summing up a known number of channels in the γ spectrum obtained. Figures 1-2 show examples of the γ spectra of neutron-activated crude and bleached oil showing the presence of phosphorus and selenium, and selenium, respectively. The spectra were obtained 1.5 months after the irradiation.

RESULTS AND DISCUSSION

The results of the selenium, arsenic, bromine and phosphorus determinations, carried out on samples of raw

TABLE II

Selenium and Bromine Content in Samples of Oil Taken at Different Stages in the Refining and Hydrogenation Process

	Mackerel						Herring					
	Stored 0 days		Stored 6 days		Stored 13 days		Stored 0 days		Stored 6 days		Stored 12 days	
Sampling stages	Se, ppm	Br, ppm	Se, ppm	Br, ppm	Se, ppm	Br, ppm	Se, ppm	Br, ppm	Se, ppm	Br, ppm	Se, ppm	Br, ppm
Crude oil	0.09	4.5	0.15	4.2	0.28	3.9	0.05	3.7	0.19	3.7	0.21	3.2
Alkaline-refined oil	0.05	4.7	0.09	4.0	0.24	3.6	0.04	3.3	0.14	3.6	0.16	3.3
Bleached oil	0.05	3.7	0.09	3.9	0.19	3.3	0.04	3.0	0.12	3.3	0.15	3.6
Hydrogenated oil, 10 min	<0.02	0.6	<0.02	0.7	<0.02	0.7	<0.02	0.6	<0.02	0.7	0.02	1.2
Hydrogenated oil, 25 min	<0.02	0.4	<0.02	0.4	<0.02	0.6	<0.02	0.3	<0.02	0.3	<0.02	0.9
Hydrogenated oil, 60 min	<0.02	0.3	<0.02	0.4	<0.02	0.6	<0.02	0.2	<0.02	0.5	<0.02	0.8
Hydrogenated oil, 120 min	<0.02	0.3	<0.02	0.2	<0.02	0.4	<0.02	0.2	<0.02	0.2	<0.02	0.5

oil produced from the same raw material which had been stored at different lengths of time, are shown in Table I. Even though relatively few samples have been analyzed in each series, the results indicate that a significant increase in the amount of extractable selenolipids occurs, during this period of storage. The results also indicate that the main release of these selenolipids from the tissue and into the extractable oil phase takes place after 4-6 days storage. The extraction of phospholipids seems to follow the same pattern. From a relatively low level of 2-10 ppm phosphorus in the beginning of the storage period (0-4 days), the content increases with a factor of 5-10 during the next 5-6 days. In the case of bromine, the results show that the content of this element is approximately constant in oils produced from the same raw material. This is in accordance with earlier results which show that brominated compounds are distributed among both polar and nonpolar lipids (5). Even the content of arseno compounds does not seem to be dependent upon the quality of the raw material from which the oil is produced, in spite of the fact that the arseno organic compounds must be characterized as typical polar lipids. No absorption of these compounds to the tissue seems to take place in the same way as with the seleno and phospholipids.

The results of the bromine and selenium analyses of the oil samples taken at different stages during the processing of the oil are presented in Table II. They also confirmed that the phospholipids and the arseno organic compounds are washed almost quantitatively out during the alkaline treatment. Neither bromine nor selenium are removed during the alkaline-refining and the bleaching of the oil. Here the selenium content is only reduced to about one-third. In the case of bromine, the different refining steps seem to have little or no effect.

During the hydrogenation process a significant fall in both the selenium and bromine contents is observed. This is most pronounced for the selenium, which disappears almost completely already after a hydrogenation period of 10 min. The bromine disappears more slowly. However due to a considerable higher content, the bromine compounds may have a more pronounced effect on the catalyst as an inactivating agent.

On the basis of these results one can conclude that both bromine and selenium organic compounds present in marine oils seem to have an inactivating effect on the catalyst during the hydrogenation of the oils. The bromine content of the oils will in the main be independent of the quality of the raw material from which the oil is produced, while the content of the selenium will increase as the raw material deteriorates. Since the presence of corresponding selenium and bromine organic compounds in vegetable oils has not been detected, the effect of these compounds will be a characteristic of marine oils when they are hydrogenated.

ACKNOWLEDGMENT

The Norwegian Herring Oil and Meal Industry Research Institute, the Department of Industrial Chemistry, and the Norwegian Institute of Technology, University of Trondheim, provided samples used in this study.

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[Received August 25, 1972]