Letter to the Editor

Variations of Trace Metal Content of Edible Oils and Fats During Refining Processes

Sir:

Interest in the occurrence of traces of heavy metals in oils and fats has increased notably in recent years. This interest derives from the association of trace metals with the origin of oils (soils and fertilizers), metal processing equipment, catalysts used for hydrogenation and, more importantly, from the effects of trace metals on the characteristics of finished products (1-3).

Exact determination of traces of metals is a major step in evaluating and testing oils and fats, specially edible grades (1, 2). It is very important to precisely determine catalytic metals that promote oxidation at ordinary temperature, namely Cu, Fe, Cr, Mn, Co and Ni (1, 3). Minute traces of catalytic metals directly affect "useful life," or "keeping time," of edible fats (4, 5), due to the acceleration of atmospheric oxidation that causes off-flavor or off-taste development. As little as 0.1 ppm Cu in margarine is said to be deleterious to flavor stability on storage (1). On the other hand, the detection and evaluation of environmental contamination of food materials by toxic heavy metals, such as Pb, Hg, Cd and Cr, is becoming increasingly important (1).

We believe that alkali treatment considerably reduces the concentration of most trace metals existing in crude oils (2). It was suggested by local oil industry experts that detectable increases of trace metal content may occur during other stages of refining due to the corrosion of processing equipment and metal containers at higher temperatures, or through the use of different bleaching earths and different catalysts. Sn, Cu and Ni are components of common catalysts used in oil technology and must be removed from the finished products (1).

It was therefore necessary to investigate the variations in trace metal content during alkali refining, bleaching, hydrogenation and deodorization.

Using a direct aspiration method of atomic absorption spectrometry, similar to the procedure described by L.T. Black (6), we have precisely determined traces

TABLE 1

Determination of Trace Metals in Oil Samples Taken from Different Stages of Refining and in Standard Oils[a]

Sample	Cu	Fe	Cr	Ni	Pb	Zn	Mg	Ca
Nab Vegetable Oil Factories								
Crude soybean	<0.005	0.37	<0.10	1.0	1.5	0.30	43	15
Alkali refining	<0.005	0.12	<0.10	1.2	1.6	<01	<0.01	<0.10
Bleaching	<0.005	0.12	<0.10	1.0	1.4	0.06	0.37	<0.10
Hydrogenation	<0.005	0.12	<0.10	1.8	1.5	<0.01	0.20	<0.10
Deodorization	<0.005	0.12	<0.10	1.2	1.5	0.06	<0.01	<0.10
Behshahr Industrial Group								
Crude soybean	<0.005	0.37	<0.10	0.75	1.5	0.06	30	16
Alkali refining	<0.005	0.12	<0.10	0.75	1.5	0.06	0.35	<0.10
Hydrogenation	<0.005	0.12	<0.10	1.2	1.5	<0.01	0.25	<0.10
Deodorization	<0.005	0.12	<0.10	0.75	1.5	0.06	0.50	<0.10
Finished shortening	<0.005	0.12	<0.10	0.75	1.5	<0.01	<0.01	<0.10
Jahan Vegetable Oil Refinery								
Crude cottonseed	0.020	6.0	0.20	1.0	1.2	1.0	107	30
Crude soybean	0.20	0.30	0.20	<0.1	0.85	0.60	6.2	27
Alkali refining	<0.005	0.10	<0.10	1.0	1.2	0.30	1.8	6.0
Hydrogenation	<0.005	<0.05	<0.10	2.0	1.0	0.15	<0.01	<0.10
Deodorization	<0.005	<0.05	<0.10	1.75	1.0	0.10	<0.01	<0.10
Finished oil	<0.005	0.10	<0.10	1.0	1.0	0.10	0.04	<0.10
Finished shortening	<0.005	<0.05	<0.10	1.75	1.0	0.10	<0.01	<0.10
Narguess Vegetable Oil Refinery								
Crude oil	0.01	0.30	0.20	<0.10	1.0	0.40	3.0	14
Alkali refining	<0.005	<0.05	<0.10	<0.10	1.0	0.15	0.03	<0.10
Bleaching	<0.005	<0.05	<0.10	<0.10	1.0	0.15	<0.01	<0.10
Hydrogenation	<0.005	<0.05	<0.10	0.80	1.0	0.15	<0.01	<0.10
Deodorization	<0.005	<0.05	<0.10	0.80	1.0	0.15	<0.01	<0.10
SP1	0.95	1.05	0.90	1.10	1.0	1.0	1.0	1.0
SP4	4.0	4.0	4.0	3.95	3.8	4.1	4.0	4.1

[a] Expressed in ppm.

of Cu, Fe, Cr, Ni, Pb, Zn, Mg and Ca in oil specimens provided by four modern refineries producing the best edible oils and shortenings of this country. Samples of raw materials, alkali treated oil, oil after bleaching, oil hardened by hydrogenation and deodorized oil were carefully analyzed.

EXPERIMENTAL

Equipment. A Varian Techtron Model 1000 atomic absorption spectrometer was used for our determinations. This AAS unit is equipped with logarithmic signal output and a variable scale expansion capability up to 10 × magnification. Varian techtron hollow cathode lamps were used as light sources.

Procedure. We have adopted the method of direct aspiration using redistilled methyl isobutyl ketone (MIBK) as solvent. The sensitivity and limits of detection of this technique are satisfactory for most metallic impurities encountered in edible oils (6).

Fifteen g oil sample is dissolved in MIBK, diluted to 25 ml in a volumetric flask and directly aspirated into the flame. This solution has an optimum aspiration speed of two ml/min.

SP Oil Standards were used for plotting calibration curves. These oil standards are prepared by addition of the calculated weights of special organometallic chelates to the base oil (6, 7). SP1 and SP4 contain 1 ppm and 4 ppm, respectively, of each trace metal. These Standards are obtainable from Cannon Instrument Company, State College, Pennsylvania.

RESULTS AND DISCUSSION

Our results are listed synoptically in Table 1. The following statements may be made from the study of tabulated data:

(i) Alkali refining considerably reduces the concentrations of Cu, Fe, Cr, Zn, Mg and Ca in crude oils. However, Pb and Ni contents seem to remain the same through this operation.

(ii) In the adsorptive bleaching step the concentrations of Mg and Ca, and all other trace metals, change very little.

(iii) During hydrogenation the amount of Ni dissolved in oil is increased due to the addition of Ni catalysts. Mg and Ca are decreased in samples coming from three refineries. All other traces remain the same.

(iv) During deodorization, variations of trace metal content are not reproducible.

Respecting traces of Cu, Bailey's book (1) states, "Maximum levels should be below 0.02 ppm for good product stability." Hochstadt (4) says, "The keeping time of lard is reduced by one-half by 0.05 ppm Cu and 1.20 ppm Fe. Cu and Fe are therefore the worst offenders, as far as atmospheric oxidation is concerned."

The oil samples that we analyzed (Table 1) all contained less than 0.005 ppm Cu after alkali treatment. It is reasonable, therefore, to recommend a new tolerance of 0.01 ppm Cu for good quality products. Similarly, we may recommend an allowable limit of 0.10 ppm for Fe.

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