This same general method has been used to good advantage in the preparation of quantities of high purity stearic and palmitic acids. In the case of stearic acid the raw material containing 80% stearic and 20% palmitic acids by weight was melted and dissolved in isopropanol in the weight ratio of 1 part of acids to 8.3 to 9.4 parts of alcohol at about 130°F. This solution was cooled to 50°F. and filtered in the same manner as the wool grease, except that the cake was washed continuously on the filter drum with cold alcohol. Stearic acid product of 92 to 96.5 weight % purity was prepared by this method. In the preparation of palmitic acid, acetone was used as the solvent, and the raw material was dissolved in the weight ratio of 1 part of acids to 12 parts of acetone at 100°F., cooled at 35°F., filtered, washed, and stripped of solvent. Palmitic acid having purity greater than 90% was produced.

Experience in preparing the three products described has shown that the method of fractional crystallization employing the 55-gallon drum is of value in making large samples of certain new products for evaluation prior to installation of integrated pilot-plant facilities. Also the information gained in handling the raw materials and final products in the improvised equipment has been of considerable aid in pointing out a more practical approach to the design of final pilot-plant equipment.

Spectrochemical Determination of Iron and Copper in Commercial Oils[1]

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ESTABLISHMENT of the relationship between copper and iron content and flavor stability of salad oils required an analytical method for these elements with a sensitivity of approximately 0.01 p.p.m. This sensitivity was estimated from flavor changes caused by additions of small quantities of copper and iron compounds to an oil which had exceptional flavor and storage qualities. Since the amount of sample available for metal analysis often was limited, a method was desired from which duplicate results for both copper and iron could be obtained on 100 grams of oil or less. The spectrochemical method was selected because of its sensitivity and specificity. Analyses have shown that some oils contain less than 0.01 p.p.m. copper whereas the iron content of all oils analyzed has exceeded this concentration.

Attempts were made to analyze the oil directly in the arc, a method which is used for additives in lubricants (1), but it was found that this method did not have sufficient sensitivity.

O'Connor (5) has published a spectrochemical method for determining as low as 0.1 p.p.m. copper and iron in oils. We have modified his ashing technique so that duplicate results for both copper and iron may be determined on a 40-gram oil sample containing as little as 0.001 p.p.m. copper and 0.01 p.p.m. iron.

Wet ashing methods, which are widely used on organic materials, were found to be unsatisfactory in this instance because of the large amounts of mineral acids necessary, the size of container required to carry out the decomposition, and the difficulty of reducing the volume of the resulting solution.

It is well known that elements other than those being determined may influence the intensity of the spectral lines of the elements of interest. For this reason a semi-quantitative analysis of 16 different commercial oils from seven companies was carried out to determine the major metallic constituents. The ash was found to be composed of calcium, magnesium, and sodium compounds in varying relative amounts. Each of these was found to enhance the intensities of the iron lines several-fold and the copper lines to a lesser extent.

The ash content of two commercially refined oils was determined and found to be approximately 30 p.p.m.; by contrast the ash content of seven laboratory-refined oils was found to be 10 p.p.m. or less (6). In order to overcome the variability caused by the approximately 0.5 mg. ash obtained from 20 grams of commercially refined oil, calcium, magnesium, and sodium nitrates were added to each oil sample before ashing. These salts were chosen for their solubility in organic solvents, as well as for their decomposition in the presence of organic material, to form a matrix consisting of carbonates and oxides. This addition increased each of the major metallic constituents to such a level that the small variation caused by the ash no longer has an effect on line intensity. The matrix also acts as a carrier for the extremely small amount of ash obtained from many refined oils. In the case of many laboratory-refined oils it was impossible to see the ash resulting from 20 grams of oil.

Preparation of Ash and Standards

Oil samples of 20 grams or less were weighed into 100-ml. Pyrex beakers. In the case of crude oils the sample weight required has been as low as 0.50 gram. An internal standard, consisting of 5.88 x 10⁻³ mg. beryllium nitrate in methyl ethyl ketone together with 4.9 mg. calcium nitrate, 3.7 mg. magnesium nitrate, and 1.6 mg. sodium nitrate dissolved in methyl alcohol, was added to each sample before ashing. The samples were then partially decomposed by slow pyrolysis on a hot plate. The initial hot plate temperature was approximately 350° C. and was increased stepwise to 450°C. Pyrolysis was carried out at a rate sufficiently slow to avoid mechanical loss of sample by spraying and violent bubbling. Treated in this manner, the samples seldom burst into flame; however analyses have shown no appreciable loss of copper or iron in those samples which did ignite. Decomposition on the hot plate required approximately 18 hours. The charred samples were then transferred to a muffle furnace and ashed at 450°C. The ashing

temperature was kept low to avoid volatilization of copper and melting of the ash. The total ash for each sample was used for analysis although quantitative recovery is not required because of the use of a reference element.

Standards used for the calibration curve contained a constant amount of beryllium and known amounts of copper and iron. The standards were prepared by drying solutions containing these elements into a matrix with the same approximate composition as that obtained from oil samples. The matrix used for each standard was 3 mg. calcium carbonate, 1 mg. magnesium oxide, and 1 mg. sodium carbonate, which contains the same amounts of calcium, magnesium, and sodium as that added to each oil sample before ashing.

Preparation and Evaluation of Spectrogram

Quantitative emission spectrochemical analysis and, specifically, the internal standard method are adequately described in the literature (4). Only the essential working conditions are given here.

All of the ash from an oil sample was transferred to an inch length of ¼-inch pure graphite electrode with a well 5 mm. deep drilled in one end. The inside diameter of the well was 5.0 mm., with walls 0.5 mm. thick. The sample was made the anode in a 13-ampere direct current arc, and the electrode separation was held constant at 5 mm. throughout the 2-minute exposure necessary to completely volatilize the sample. Lengths of ⅛-inch pure graphite electrodes were used as cathodes. The spectrum was photographed on "Eastman 33" plates, using a large Littrow spectrograph with a slit width of 12.5 microns. A step sector and an intensity sector, set to eliminate one-half the emitted light, were used with each exposure. Plates were developed 5 minutes at 20°C. in Eastman D-72 developer. Opacities of the copper, iron, and beryllium lines shown in Table I were measured

TABLE I
Spectrum Lines Selected for Analysis

Element	Line identification (Angstrom units)	Calibration range (Micrograms in arc)
Beryllium	3131.1	Internal Standard 0.4
Copper	3247.5	0.032-10
Iron	3020.6	0.38 -100
Iron	3057.4	5-100

in a densitometer and converted to relative intensities from an emulsion calibration curve obtained from each plate. The range over which each line is calibrated is shown in the table. Ratios of relative intensities of the iron or the copper line to beryllium were then converted to concentration from the calibration curves shown in Figure 1.

Results and Discussion

Copper and iron content of several representative oils are shown in Table II. Results are based on duplicate determinations unless these did not agree within 30% of the mean, in which case a third trial was made on that sample. For the first 225 oils analyzed the average precision was found to be 18%. Table II also contains the extremes in copper and iron content observed. The method was used for determining the copper and iron content of oils in the
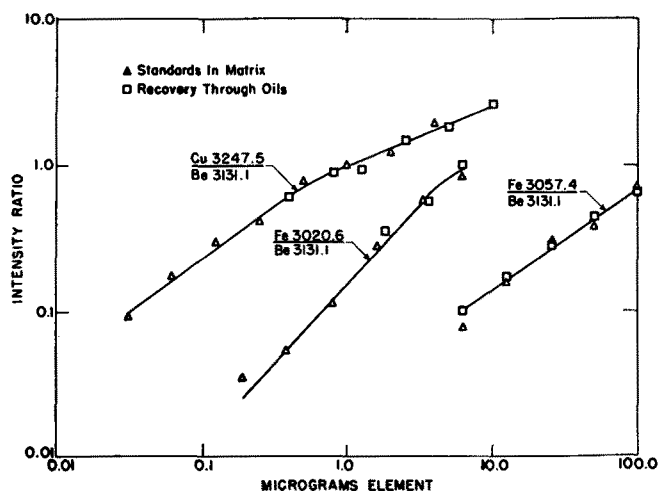

FIG. 1. Calibration curve.

TABLE II
Copper and Iron Content of Representative Commercial Oils

Oil No.	Oils	Copper, p.p.m.	Iron, p.p.m.
Crude oils:			
1	Corn oil	0.50	12.7
2	Soybean oil	.13	2.3
3	Soybean oil	.10	5.6
Commercial salad oils:			
4	Soybean oil	0.045	2.50
5	Soybean oil	.0064	0.077
6	Soybean oil	.0050	.08
7	Cottonseed oil	.016	.16
8	Corn oil	.015	.10

publications of Evans, et al. (2, 3, 6), on the flavor problem of soybean oil.

As a test of the accuracy of the procedure, known amounts of copper and iron compounds were added to an oil which had been shown to contain only relatively small amounts of copper and iron. Results of the recovery are indicated in Figure 1 with the calibration curve. The recovery of iron and copper was quantitative to within ±8% and ±10%, respectively. Since the average of numerous trials on known samples used to construct the calibration curve was ±10% of the amount known to be present, the recovery of added copper and iron was considered satisfactory.

Summary

Application of the internal standard method to the spectrochemical analysis of oils in conjunction with the use of a modified ashing technique has been shown to permit quantitative determination of copper to 0.001 p.p.m. and of iron to 0.01 p.p.m.

The procedure has been tested by the addition of known amounts of copper and iron to oils and recovery has been found satisfactory.

Results on several commercial oils are given to illustrate the range over which the method is applicable.

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