# Char-Ashing of Glyceride Oils Preliminary to the Atomic Absorption Determination of Their Copper and Iron Contents[1]

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## ABSTRACT

Trace amounts of copper and iron were determined by char-ashing samples of molecularly distilled glyceride oil, copper hydrogenated edible oils and salad oils with added copper salts and copper-chromite catalysts. Char-ashing, coupled with the atomic absorption method of analysis, gave excellent reproducibility in a salad oil for copper at 0.025 ± 0.002 ppm and for iron at 0.082 ± 0.012 ppm. Agreement was excellent between the char-ashing method and the direct solvent method of analysis when levels of the two trace metals were high enough to be analyzed by direct atomic absorption. Copper in edible oils can be accurately analyzed at levels of less than 10 ppb by the char-ashing technique.

## INTRODUCTION

List et al. (1) have shown that the direct method (oil samples are dissolved in solvent and aspirated directly into the flame) for the determination of copper by atomic absorption at low levels (0.05-0.40 ppm) in edible oils was sensitive and had a low standard error. Burrows and coworkers (2) found good agreement between ashing and the direct determination of copper at levels of 1.0-40 ppm in lubricating oils. They also determined iron (3-55 ppm) by both methods and, generally, found good agreement between them. In the few examples they cite of ashing, always at high levels, that technique gave higher, never lower values than the direct solvent method. The higher levels in ashing may be attributed to particulate iron matter because Bartels and Slater (3) showed that only iron particles below 10 μ in diameter contribute to absorption in the flame. Others have used direct solvent determination for lubricating oils (4,5) and also for edible fats (6). Ashing glyceride oils by official AOCS methods (7) consists of igniting the hot oil with a flame and supplying sufficient heat to keep the sample burning. This ashing method unfortunately gives consistently low results (8,9). Deck and Kaiser (10) recently reported recoveries of copper ranging from 0-84%. Ashing, like weighing, is a fundamental operation and if handled correctly will yield accurate results. We prefer the terminology of char-ashing to describe our method and to distinguish the pre-ashing step from direct burning and ashing, terms which have been previously used.

Because of current interest in copper catalysts to hydrogenate edible fats (11-13) it was deemed desirable to check the direct solvent method against the char-ashing method. Since copper-chromite catalysts are exceedingly fine, mostly below 2 μ in size, and are removed with difficulty from oil after its hydrogenation, the possibility that copper may exist in hydrogenated oils as particulate matter must be considered. Any copper present as particulate matter will be determined by ashing but may not be by the direct solvent method.

Any ashing of fats is a tedious and lengthy task since the oil must first be completely carbonized on a hotplate before it is ashed in an electric muffle furnace. In the char-ashing technique carbonization must be controlled so that the oil does not reach the fire point. The amount of oil that can be readily ashed by charring is limited, usually no more than 200 g. The entire char-ashing process takes about 2 days to prepare a sample for analysis. In the direct method, sample preparation requires only that time necessary to make up a 10% or 25% by weight oil solution in methyl isobutyl ketone. The one difficulty of the direct method for low-level metal determination is obtaining a metal-free oil from which to prepare standards.

## MATERIALS AND METHODS

The soybean oil used was a commercial sample of a nonhydrogenated salad oil. This sample, selected because of its low metal content, has been used to make up standards

TABLE I

Reproducibility and Metal Recovery by Char-Ashing

| Sample | Copper, ppb | Iron content, ppb | | |
|---|---|---|---|---|
| Soybean salad oil<br>(not hydrogenated) | 26 | 54 | 87 | 73 |
| | 22 | 79 | 80 | 90 |
| | 26 | 95 | 73 | 93 |
| | 27 | 93 | 93 | 100 |
| | 27 | 76 | 76 | 74[a] |
| Average | 25 ± 2 | | 82 ± 12 | |
| Soybean salad oil plus metal | 555 Cu | | 582 Fe | |
| Total | Found 546 | | Found 513 | Found 522[b] |
| | 534 | | 515 | 570 |
| | 537 | | 510 | 555 |
| | 528 | | 500 | 550 |
| | 543 | | 500 | 523 |
| | 552 | | 505 | 535 |
| | 540 ± 8 | | 507 ± 6 | 543 ± 17 |

[a] There was more iron analysis than copper because some samples in this series were spiked with copper.

[b] Different operator and different spectrometer.

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[1] Presented at AOCS Meeting, Atlantic City, October 1971.

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TABLE II

Comparison of Vycor and Porcelain Dishes as Ashing Vessels

| Sample | Copper content, ppb | | | | | | Iron content, ppb | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Vycor | | | Porcelain | | | Vycor | | | Porcelain | | |
| Soybean salad oil | 25[a] | | | 80 | 230 | 220 | 82[b] | | | 90 | 95 | 73 |
| Copper hydrogenated soybean oil | 8 | 8 | 12 | 130 | 110 | | 150 | 120 | 180 | 210 | 210 | 230 |
| Copper catalyst[c] residue in oil | 320 | 290 | 310 | 190 | 460 | | 54 | 87 | 73 | 90 | 95 | 73 |
| Copper hydrogenated + $Mg(NO_3)_2$ | --- | --- | --- | 20 | 130 | | --- | --- | --- | 95 | 120 | |

[a] Average of 5 samples

[b] Average of 15 samples.

[c] Copper-barium-chromite catalyst.

as well as samples containing copper oleate, copper chlorophyll and catalyst residues left after hydrogenation of soybean oil with copper catalysts.

Copper hydrogenated oil was from a specially prepared lot of soybean oil commercially hydrogenated with a commercial copper-barium-chromite catalyst.

Copper oleate, copper chlorophyll and magnesium nitrate were purchased commercial chemicals. Copper standards were made up in soybean oil from a sample of National Bureau of Standards chelate, bis(1-phenyl-1,3-butanediono) copper II No. 1080, according to their directions.

### Char-Ashing

In a 350 ml Vycor dish, 150 g of oil was weighed out (50 g in a 100 ml dish) and charred on a full-heat-controlled hotplate (Thermolyne Model 3423-1, 1685 watts). The usual three-stage heat control hotplates was not entirely satisfactory as full heat ignites the sample and medium heat is too slow. Carbonization of the fat was conducted on as high a heat as possible (approximately 300 C) but below ignition temperature; under these conditions usually about 24 hr were required for complete charring.

The fire points of various glyceride oils are reportedly between 246 and 363 C (14). Charring on the hotplate is complete when the sample stops smoking and no longer appears oily. Oil samples charred to this extent will not puff and froth from the dish when placed in a muffle furnace. Charring should not be carried to the stage of actual ashing on the hotplate as air convection currents tend to carry off the ash.

After charring, dishes were ignited in a lined muffle furnace at 500 C for 16 hr. The muffle temperature must be carefully controlled as high heat will cause loss and open heating element furnaces may scale and cause errors in low level analysis. Porcelain dishes were not satisfactory as high and variable results were experienced; this discrepancy was especially true if the dishes were rough and showed signs of flaking. Analytical errors caused by porcelain glaze in trace copper analysis have been known for a long time (15). All results reported here, except those where porcelain dishes are compared, were obtained with new Vycor dishes.

Ash from edible oil is extremely fine and dishes were allowed to cool before removing them from the muffle furnace. The ash was dissolved in 10 ml of 5% high-purity sulfuric acid (G. Fredrich Smith No. 273 double-distilled in Vycor). A 30 min acid digestion of the ash was carried out on a steam plate and then the sample was carefully washed with double-distilled water into a 25 ml volumetric flask. A second digestion with 5 ml of acid was also performed and the contents added to the volumetric flask, which was made to volume with water.

A blank sample was carried through the entire char-ashing and digestion steps and the atomic absorption corrections were made from this blank. Samples and blanks were aspirated directly into the atomic flame without further dilution or concentration.

### Direct Method

Ten grams of oil were weighed into a 50 ml, glass stopper Erlenmeyer flask and dissolved in 30 g of redistilled methyl isobutyl ketone (bp 115-116 C). The samples were equilibrated to 40 C and aspirated into the atomic absorption flame at this temperature. All samples were run on a Perkin-Elmer 303 atomic absorption spectrophotometer equipped with a three-slot titanium Boling burner. Details of this operation have been reported (1).

## RESULTS

Reproducibility of analysis was good for both copper and iron at low levels by the char-ashing technique on 50-150 g of oil. These metals are always found in trace

TABLE III

Comparison of Methods for Analysis of Copper

| Sample | Copper content, ppb[a] | | |
|---|---|---|---|
| | Calculated | Direct aspiration | Char-ashing |
| Soybean salad oil | --- | N.D.[b] | 25 |
| Copper hydrogenated soybean oil | --- | ⟨ 20 | 9 |
| Catalyst residue in oil | --- | 325 | 308 |
| Copper chelate[c] in oil | 345 | 360 | 369 |
| Copper chlorophyll in oil | 1,320 | 1,320 | 1,320 |
| Copper oleate in oil | 500 | 550 | 540 |
| Molecular distilled oil[d] | --- | ⟨ 20 | 18 |

[a] Triplicate analysis.

[b] N.D. = not detected.

[c] Bis(1-phenyl-1,3-butanediono) copper II—NBS No. 1080.

[d] Distilled herring oil—iron by char-ashing in this sample was 60 ppb.

amounts in salad oils. Table I shows results with a standard deviation of only ±2 ppb for levels of 25 ppb copper. The reproducibility for iron was not so high but still was good at levels of 82 ppb ±12. For added metals (approximately 0.5 ppm) recovery and reproducibility for copper were also better than for iron. The coefficient of variation for the added copper was 14.8% and for added iron was 11.8% and 32.2% for two analysts. The percentage recovery of the added copper was 97.9% and for added iron was 87.2% for one operator and 93.2% for the other. Considering the levels at which these metals are being analyzed, the char-ashing technique has given acceptable analyses. Our results would indicate that the low ashing recoveries reported in the literature were caused by improper ashing conditions. It seems quite doubtful that active burning of the sample can be used to ash glyceride oils because loss of iron and copper is excessive.

Data in Table II show the variable results for copper and iron obtained by ashing the samples in porcelain dishes. The variability of iron was not so great as for copper, but the analyses for copper and iron in porcelain are much higher than for the same samples ashed in Vycor. Since the porcelain dishes were not new, probably some of the variability would be attributed to dishes that had lost their glaze. All Vycor dishes were new at the start of this investigation. Since magnesium nitrate is commonly employed when ashings are conducted in platinum dishes, a few ashing determinations were made with this oxidant. Ashings were conducted with 0.4 g of $Mg(NO_3)_2$ per 100 g of oil. Since copper blanks were exceedingly high and since there was no evident advantage, the use of magnesium nitrate with porcelain or Vycor dishes was not continued.

Table III compares the char-ashing technique with direct aspiration of an oil sample solution into an atomic absorption spectrophotometer. Again it is shown that char-ashing is reliable and that it gives nearly total recovery of copper present in an oil. The method has the additional advantage of allowing analysis for trace metals at a much lower level than direct aspiration. The usefulness of char-ashing technique permits determination of trace metal contents of molecularly distilled glyceride oils. Because char-ashing is more sensitive, it can also be used to analyze the metal contents of oils that are used to standardize atomic absorption spectrophotometers for the direct aspiration technique. The char-ashing method appears suitable for the determination of a few parts per billion of iron or copper in edible fats with high accuracy.

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