A Rapid Method for the Determination of Trace Cu and Fe in Edible Salad Oil by Graphite Furnace Atomic Absorption Spectroscopy

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In the determination of trace amounts of copper and iron in edible salad oils by graphite furnace atomic absorption spectroscopy (GFAAS), an ashing method with low temperature oxygen plasma was used to effectively eliminate the interference of the organic matrix. Two sample preparation methods were studied, extraction with concentrated nitric acid followed by ashing with the low temperature oxygen plasma to determine the yield of extraction, and direct analysis of the metal content after dilution with methyl isobutyl ketone (MIBK). Results obtained from these methods were compared with the background absorbance by inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

During the processing of edible salad oils, catalysts (Cu and Fe) are sometimes added during hydrogenation to reduce linolenic acid (1). If the Cu and Fe contained in edible salad oil exceed 100 ng/g, they cause oxidation to continue, deteriorating the quality of the oil and producing a displeasing odor (2,3). It is difficult to remove metallic compounds completely during processing if the diameters of the particles are under 2 μm (4). Therefore, routine analyses for traces of Cu and Fe are necessary in edible salad oils. After having been through wet digestion, high pressure bomb digestion or microwave heating with acid digestion, samples usually will have residues on the top layer of fat. The residues are hard to dissolve with strong acids (such as nitric acid) by either the charring method (3-6), the organic solvent dilution method (6-8), or even by the less complicated method of mixing the extract with concentrated nitric acid (9). The most favored pretreatment method is the high temperature ashing method in which the organic substance can be removed completely; however, many papers (5,7-10) report that this method still has disadvantages due to complicated steps that lead to systematic errors.

Since first introduced by Thomas (11), the method of low temperature oxygen plasma ashing has gained wide popularity because it can remove the organic matrix completely. But the ashing process still takes a long time, because this method depends on oxygen without resorting to any added reagent. The oxygen plasma is oxidized to ash at a low temperature range (50-180 C) to remove interference from organic substances; this is similar to the analysis of metal content in water. Edible salad oils, when dried by suction, will form a strong, brown, glue-like substance which will limit the rate of ashing by blocking the passage of the oxygen plasma. Although the ashing process can be accelerated by adding filter paper and powdered corn starch as proposed by List et al. (12) and Tamura et al. (13), they are hard to obtain in high purity. Results obtained by List et al. that are far below those obtained by other methods may be attributed to the loss resulting from the high ashing power (180-200 W) (14).

By dilution of samples with kerosene, Dijkstra et al. (7) obtained very good results; the metal contents are analyzed directly by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). In order to reduce equipment costs and fuel consumption, a low temperature oxygen plasma ashing method was explored in the present experiment. It was applied to edibloe salad oils that had been diluted with methyl isobutyl ketone (MIBK) and then analyzed by graphite furnace atomic absorption spectroscopy (GFAAS).

In order to study the feasibility of extraction with concentrated nitric acid or concentrated nitric acid with hydrogen peroxide, we analyzed the acid solution after extraction and the top layers of the residues.

EXPERIMENTAL

Reagents and containers. Water used in this experiment was deionized, treated with active carbon and antiosmosis, and then deionized again. Finally, it was distilled through a two-section quartz distiller. All reagents used are of E. Merck's analytical reagent grade. The standard solutions were E. Merck Tritisol-9987 and 9972 aqueous solutions for Cu and Fe, respectively, and E. Merck Art. 15055 and 15068 oil standard for Cu and Fe, respectively. The containers were made of pyrex, quartz or teflon. Containers were soaked in 6N nitric acid overnight and then washed with water.

Apparatus. The low temperature oxygen plasma asher (LTA) was a Branson/IPC 1000 with a radiofrequency ware of 13.56 MHz, 550 W Maximum output and or 800 1/min vacuum pump. For graphite furnace atomic absorption spectroscopy (GFAAS), the main body was an Instrumentation Laboratory IL-257 model with a D_2 lamp for background correction, an IL-555 Atomizer and an IL-FASTAC 254 automatic sampler. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was done with a Kontron AGS-35 (sequential series). The radio frequency was 3.5 KW, spectrum 200-500 nm, grating dimension 80 × 100 mm, linear dispersion 0.6 nm/mm and optical resolution (FWHM) 0.015 nm.

Sample processing. For the low temperature oxygen plasma ashing method, a 3-4 g sample of edible salad oil was weighed into a quartz dish 3 cm high and 6 cm in diameter. The dish was placed in the low temperature ashing furnace, and the air inside the furnace was pumped out slowly for one hr, followed by a faster rate for four hr to maintain the vacuum below 0.1 Torr. The volume of the sample did not exceed one-tenth that of the ashing dish, because thick layers of salad oil cause bubbles that can overflow from the dish. Samples were completely ashed under an oxygen flow

rate at 250 ml/min at several radio frequencies. The color of the oxygen plasma turns from bright blue to dark pink indicating that ashing is completed. About 40-48 hr are required to ash eight 4-g samples. The sample was removed, dissolved in 10 ml 0.1N nitric acid, and then applied directly with GFAAS to determine its metallic content.

For acid extraction with nitric acid and nitric acid with hydrogen peroxide, samples (7-8 g) of salad oil were weighed into 100 ml round-bottomed flasks. To some samples 20 ml of concentrated nitric acid were added, and to others 20 ml concentrated nitric acid together with 6 ml of 35% hydrogen peroxide were added. These solutions were mixed at 800 rpm for 24 hr with a magnetic stirrer. After centrifugation, the top layer of the mixed solutions had oil residues which were ashed in accordance with the low temperature oxygen plasma ashing procedure above. The lower layer of the acid solution was diluted four times with water prior to being analyzed by GFAAS.

For direct injection after MIBK dilution, samples uniformly mixed with MIBK at a 1:2 ratio were analyzed directly by GFAAS for determination of metallic content.

An IL-254 FASTAC automatic sample injector was used to inject the samples and the standard solutions into the carbon rods for determination with GFAAS. Then, Cu was measured at 324.7 nm with a 5 mA lamp current at 530 V. Fe was measured at 248.3 nm with a 10 mA lamp current at 620 V. All other instrumental operating conditions adopted as operational manual.

RESULTS AND DISCUSSION

Investigation of the conditions for low temperature oxygen plasma ashing. When we ashed salad oils in a low temperature oxygen plasma asher, we found no water if the vacuum was near 0.1 Torr, unlike results from general biological samples. Passage of oxygen through the sample forms a film that takes 4 to 8 hr to solidify. Because salad oils are composed mainly of carbon and hydrogen, no residues were found on the dish after ashing. The metals can easily be washed out with 0.1N nitric acid and applied directly to the GFAAS.

During ashing with a low temperature oxygen plasma, the most important factor affecting the efficiency of the ashing is the input power in the radio frequency coil. Using powdered graphite (a material which has the fastest reaction rate) for an example, if the ashing power is raised from 30 W to 110 W, the corresponding temperature for the ashing is raised from 75 C to 198 C. If good ashing is to be efficiently obtained, the ashing power must be adjusted for differences in composition and forms of various biological samples. As shown in Figure 1, when the power is lower than 70 W or higher than 120 W, the ashing time changes radically. In the power range between 90 and 120 W, the time needed for ashing changes moderately. If the ashing power is too high (>120W), then there is an obvious loss of metals. The range of choice is between 90 and 110W for power and 50 and 40 hr for ashing time for

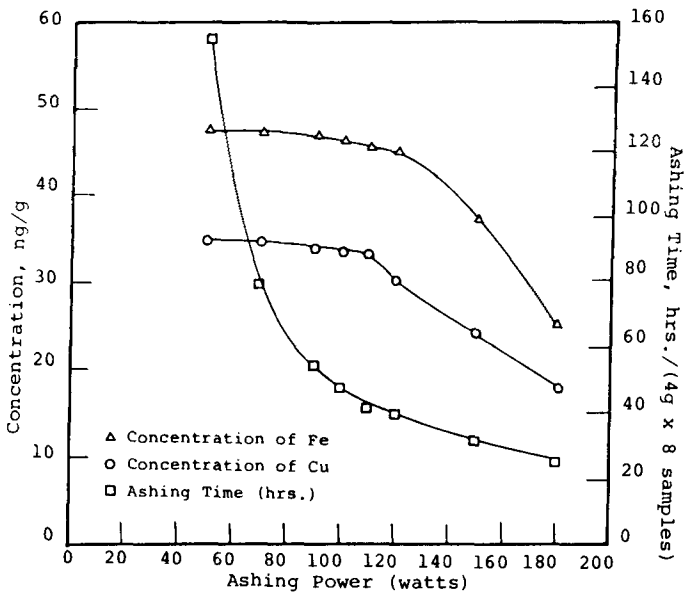

FIG. 1. Ashing times and measured concentrations at different ashing power levels of an edible salad oil.

TABLE 1

Comparison of Cu Concentration in Various Salad Oil Samples and Standard Oils Obtained by Different Pretreatment Methods

No.	Sample[b]	Cu concentration, ppb[a]			
		Low temp ashing	Conc HNO_3 extraction	Conc HNO_3-H_2O_2 extraction	Direct (MIBK dilu)
A	Soybean salad oil	33 ± 2	58 ± 2	74 ± 2	31 ± 3
B	Soybean salad oil	10 ± 1	68 ± 3	100 ± 3	11 ± 2
C	Soybean salad oil	23 ± 2	56 ± 3	65 ± 2	25 ± 3
D	Soybean salad oil	33 ± 1	57 ± 2	83 ± 2	36 ± 3
E	Soybean salad oil	16 ± 2	62 ± 3	75 ± 2	14 ± 2
F	Corn oil	27 ± 1	70 ± 2	93 ± 3	26 ± 2
G	Sunflower oil	28 ± 1	119 ± 3	164 ± 4	25 ± 2
H	E. Merck blank st'd Oil (Art. 13898)	28 ± 1	— —	— —	27 ± 2
I	E. Merck Cu-st'd oil (Art. 15055-100 ppb)	96 ± 2	— —	— —	— —

[a]Average of three independent determination.
[b]Different brands of edible salad oil purchased at supermarket.

TABLE 2

Comparison of Fe Concentration in Various Salad Oil Samples and Standard Oils Obtained by Different Pretreatment Methods

No.	Sample[b]	Cu concentration, ppb[a]			
		Low temp ashing	Conc HNO_3 extraction	Conc HNO_3-H_2O_2 extraction	Direct (MIBK dilu)
A	Soybean salad oil	46 ± 2	176 ± 3	235 ± 7	44 ± 3
B	Soybean salad oil	59 ± 2	230 ± 9	246 ± 9	62 ± 3
C	Soybean salad oil	83 ± 3	128 ± 7	173 ± 6	80 ± 3
D	Soybean salad oil	54 ± 2	97 ± 6	151 ± 7	52 ± 3
E	Soybean salad oil	121 ± 5	178 ± 7	314 ± 9	124 ± 6
F	Corn oil	78 ± 3	215 ± 5	218 ± 6	72 ± 4
G	Sunflower oil	60 ± 2	101 ± 4	137 ± 5	62 ± 3
H	E. Merck blank st'd Oil (Art. 13898)	131 ± 3	— —	— —	134 ± 5
I	E. Merck Fe-st'd oil (Art. 15068-100 ppb)	97 ± 3	— —	— —	— —

[a]Average of three independent determination.
[b]Different brands of edible salad oil purchased at supermarket.

edible salad oils. Results from analysis of seven commercial salad oils and one standard oil are shown in Tables 1 and 2.

Investigation of acid extraction with conc HNO_3 and conc. HNO_3-H_2O_2. When a salad oil is reacted with nitric acid, analysis of the spectrum can be complicated because the sample is not completely oxidized and because of interference from the acid. From Figure 2, the emission spectra of samples are compared together with background spectra. The background spectrum rose drastically from 1400 counts/s to 1900 counts/s (or from curve a to curve b) between water and 4N HNO_3. When the acid solution contains organic residues, the background rises still further. Curve c represents an aqueous standard solution and curve d a sample from which the organic substances have been removed by LTA. Curves e and f represent salad oils mixed with conc HNO_3 or conc HNO_3-H_2O_2. One can see that the emission spectra went up remarkably for curves e and f. Even the background of curves e and f exceeds the measured values of curves c and d. Results shown in Tables 1 and 2 may well explain the interference due to organic substances that cause higher measured values. After extraction with HNO_3 and HNO_3-H_2O_2, residues from the upper layers were investigated by the LTA method. Results are shown in Table 3; the extraction yield is about 60-70%. The above results show that in order to have accurate GFAAS readings, interference from organic substances should be reduced. Extraction with HNO_3-H_2O_2 shows higher measured values than with conc HNO_3 alone.

Investigation of direct analysis after dilution with MIBK. The most significant difference between analysis of a sample in an organic solvent and one resulting from solution from a mineral acid solvent is that the organic substances can be removed at low charring temperature. Thus, the possibility of loss is reduced. As shown in Figure 3 maximum absorption can be achieved at a charring temperature around 300 C. There will be no significant loss below 400 C. In a mineral

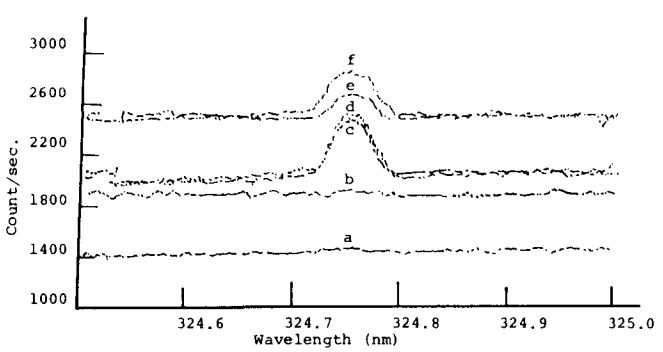

FIG. 2. Investigation of emission spectra of copper in various solution media. a, neutral pure water; b, 4N nitric acid; c, Cu standard solution, 30 ppb, in 4N nitric acid; d, salad oil sample treated by LTA followed by dissolving in 4N nitric acid; e, salad oil sample treated by nitric acid extraction followed by adjusting to 4N nitric acid; f, salad oil sample treated by nitric acid-hydrogen peroxide extraction followed by adjusting to 4N nitric acid.

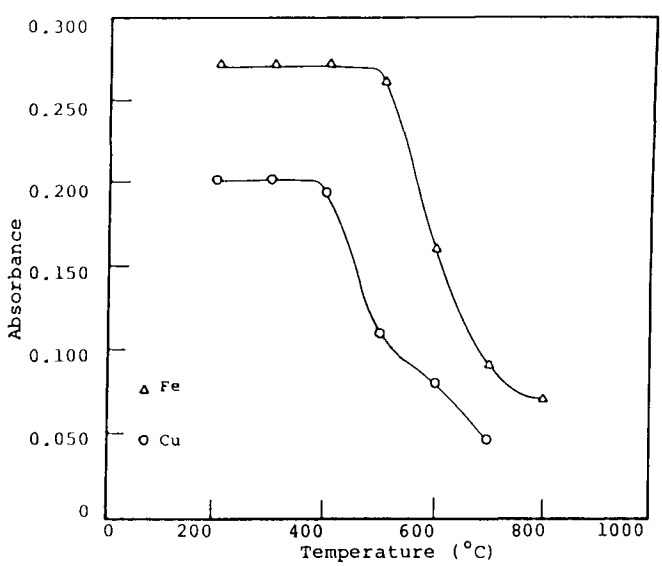

FIG. 3. Maximum charring temperature for salad oil sample after MIBK dilution.

TABLE 3

Recovery of Cu and Fe by Acid Extraction of Salad Oil and Their Contents in the Residual Oil After Acid Extraction

	Residual oil, ppb		Extraction yield, (%)	
Element[a]	conc HNO_3	conc HNO_3 + H_2O_2	conc HNO_3	conc HNO_3 + H_2O_2
Cu	13 ± 1	10 ± 1	60.6	69.7
Fe	19 ± 2	15 ± 1	58.6	67.3

[a]This sample is the same as A in Tables 1 and 2.

acid solution, the charring temperature generally exceeds 500–600 C. At such high charring temperatures, loss and incomplete ashing may occur.

From the results obtained here, the analysis of the edible salad oil can best be performed by the direct analysis method with MIBK dilution. This simple, quick and accurate method can be used in both routine work and on-line analysis.

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REFERENCES

1. Koritala, S., E. Selke and H.J. Dutton, *J. Am. Oil Chem. Soc. 50*:310 (1973).
2. List, G.R., C.D. Evans and W.F. Kwolek, *Ibid. 48*:438 (1971).
3. Mertens, W.G., C.E. Swindells and B.F. Teasdale, *Ibid. 48*:544 (1971).
4. Evans, C.D., G.R. List and L.T. Black, *Ibid. 48*:840 (1971).
5. Tsai, W.C., C.P. Lin, L.J. Shiau and S.D. Pan, *Ibid. 55*:695 (1978).
6. Ooms, R., and W. Van Pee, *Ibid. 60*:957 (1983).
7. Dijkstra, A.J., and D. Meert, *Ibid. 59*:199 (1982).
8. Olejko, J.T., *Ibid. 53*:480 (1976).
9. Van Raaphorst, J.C., A.W. Van Weers and H.M. Haremaker, *Analyst 99*:523 (1974).
10. Jacob, R.A., and L.M. Kleray, *Anal. Chem. 47*:741 (1975).
11. Gleit, C.E. and W.D. Holland, *Anal. Chem. 34*:1454 (1962).
12. List, G.R., R.L. Hoffmann, W.F. Kwolek and C.D. Evans, *J. Am. Oil Chem. Soc. 45*:872 (1968).
13. Tamura, Y., T. Ishihara and S. Moriyama, *Food and Health (Japan) 17*:477 (1976).
14. Sun, H.J., H.M. Lin and M.H. Yang, *Chemistry (The Chinese Chem. Soc., Taiwan, China) 42*:51 (1984).
15. Kahn, H.L., M. Bancroft and R.H. Emmel, *Research and Development 27*:30 (1976).

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