Ashing Techniques in the Determination of Iron and Copper in Palm Oil

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A modified method suitable for routine determination of iron and copper in palm oil was developed. The method involves all stages of ashing including charring, ashing and ash dissolution, using fabricated ashing vessels made of pyrex glass that can stand ashing temperatures of up to 700°C. The ashed samples were recovered quantitatively after refluxing with HNO_3 and collected in the attached round-bottomed flask readied for metals determination without transfer. The relative standard deviation for the determination of iron by flame atomic absorption was about 1.0%, whereas for copper determined by ion selective electrode it was about 0.5%.

Trace levels of metal ions in edible oils are well known to have serious deteriorative effects on the stability of the oils. The presence of metal ions such as iron and copper which are highly prooxidative will greatly reduce the stability of oil. Iron and copper may originate from natural sources or be introduced along the production line. The extent of metal contamination can also depend on the free fatty acids present in the oil (1). Several workers have reviewed sources of metal contamination from both the production line and the final storage tank (2–4). The metal ions can occur in suspension or be intimately incorporated in the oil. Expected concentrations of copper and iron in good quality oil usually range from 0.02 to 0.2 ppm and 2 to 5 ppm, respectively (5). At these levels of metal contamination, fast and reliable methods for their determination are very important in evaluating deleterious effects on the oils.

A number of techniques have been applied for the determination of metal ions in the oils (6,7). Wet ashing procedures which involve the mineralization of the oil using sulphuric acid and perchloric acid as oxidants have been proposed (8). Unfortunately, the application of perchloric acid to wet ashing of oils must be entrusted in skilled personnel who are fully aware of the potential danger of explosion. In view of this fact, acid extraction of the oil has been proposed by Black (9). Acid extraction can also present problems such as: (a) introduction of metal contamination if the acid is not purified prior to use, and (b) low recovery (88–92%) of the resultant metal. Therefore, dry ashing or char ashing is considered to be the better method (10). After the resultant ash has been dissolved, measurement of the metal concentration in the solution can be done by atomic absorption or ion selective electrode techniques (10). The method recommended by the AOCS involves ashing (11) prior to analysis. Direct measurements of copper using atomic absorption after dilution of the oil by an organic solvent, rather than ashing, gave a rather low sensitivity (12). With flameless atomic absorption spectroscopy lower detection limits of iron and copper were achieved by direct injection of the oil (13). Nevertheless, smoke formation during charring imposed certain limitations.

In the present work the reported procedures for ashing were investigated and appropriate modifications of the techniques were made. An apparatus is described in which all operations of ashing, including charring, ashing, ash dissolution and subsequent evaporation, result in a suitable solution for routine analysis. The ashing vessels which are made of pyrex can be attached to a reflux condenser, and the dissolved ash can be collected in a round-bottomed flask. This method resulted in better recoveries because losses of metal ions which occur due to sputtering of oil during the transfer of the ashed sample can be eliminated.

EXPERIMENTAL

Reagents. All reagents used were analytical grade. Glassware was rinsed with dilute nitric acid to remove metal contamination. Concentrated nitric acid was double-distilled before being used. Aqueous iron and copper standard solutions in dilute acid were prepared from $Fe(NO_3)_3.9H_2O$ and copper foil 99.9%, respectively. A buffer solution of pH 4–5 for the determination of copper by ion-selective electrode was prepared from $NaNO_3$, NaOH and NaI at a concentration of 0.1M, and CH_3COOH and CH_2COONa at a concentration of 0.01M.

Crude and refined palm oil samples were supplied by Palmex Industries, Malaysia.

Apparatus. A Varian Techtron (Model 1000) flame atomic absorption spectrophotometer was used for the determination of iron. A copper ion-selective electrode and a single junction Ag/AgCl reference electrode (model numbers 94–29 and 90–01, respectively, Orion Research) were used with the Orion, Model 701A for the determination of copper (the method adopted as suggested by Fung et al. [10]).

Two types of pyrex ashing vessels were used. One was a rounded cylinder and the other was a rectangular cylinder. The vessels were 23 cm long with standard taper joints to be fitted to a reflux condenser on one end and to a collecting round-bottomed flask on the other end. The diameter of the cylinder and the breadth of the rectangle were 8 cm. The effective length of the reservoir was 10 cm.

PROCEDURES

Ashing in platinum crucibles. The following three different methods of ashing were performed in a platinum crucible. The amount of palm oil used was about 50 g for each method.

(a) Flaming by bunsen burner flame until a black char was attained, then ashing at 580°C in a furnace for one hr.
(b) Flaming and ashing directly in the furnace at 350°C for two hr. followed by 480°C for three hr.
(c) Flaming and smothering of the flame with the crucible lid at one-min. intervals. During the smothering operation the bunsen was removed. This treatment

TABLE 1

Iron Content in Refined, Bleached and Deodorized (RBD) Palm Oil as Determined by AAS After Three Different Methods of Ashing

	Iron, ppm		
Replicate[a]	Flaming and ashing (Method a)	Ashing only (Method b)	Flaming, smothering and ashing (Method c)
1	1.18	1.16	1.12
2	1.20	1.18	1.13
3	1.22	1.17	1.16
4	1.17	1.18	1.13
5	1.13	1.16	1.15
Average	1.18	1.17	1.14
RSD (%)	2.87	0.85	1.45

[a]Analyses of one oil sample.

TABLE 2

Copper Content in RBD Palm Oil as Determined by Selective Ion Electrode Technique After Three Different Methods of Ashing

	Copper, ppb		
Replicate[a]	Flaming and ashing (Method a)	Ashing only (Method b)	Flaming, smothering and ashing (Method c)
1	6.80	7.50	10.00
2	7.91	7.96	7.96
3	9.42	8.90	8.30
4	12.17	7.70	6.90
5	8.30	6.80	7.90
6	30.20	8.30	8.25
7	44.44	7.62	8.16
Average	17.04	7.83	8.21
RSD (%)	85.38	8.43	11.22

[a]Analyses of one oil sample.

was followed by ashing in the furnace for two hr. at 480°C.

The resultant ash in the platinum crucible from the foregoing methods was dissolved in 10 ml concentrated double-distilled HNO_3. The acid was then evaporated on a water bath. For the determination of iron, the nitric acid residue was dissolved in 10 ml of a solution containing 0.01M $NaNO_3$ in 0.01M HNO_3 and then measured by flame AAS. For the determination of copper, the nitric acid residue was dissolved in 9 ml of the nitrate solution to which was added one ml buffer solution (pH = 4-5). The resulting solution was then made up to a 30-ml volume, and copper was determined by an ion selective electrode technique (10).

Ashing in glass vessels. An oil sample of about 50 g was poured into a preweighed ashing vessel and reweighed to get an exact sample weight. The vessel was then placed in the electric furnace at 400°C for three hr., followed by another two hr. at 520°C. The vessel was removed, cooled and 10 ml of concentrated HNO_3 was added. The vessel was rocked and rotated for effective acid coverage of the surface. Another 15 ml of concentrated HNO_3 was added, followed by additional rocking and rotating. The acid-ash solution was then collected at one end of the vessel, which was fitted to a 50-ml round-bottomed flask. A reflux condenser was then fitted to the opposite end of the condenser and the solution refluxed for 5 hr. The collected acid solution was then evaporated to dryness. The determinations of iron and copper were accomplished as described in the procedure for ashing in platinum crucibles.

TABLE 3

The Recovery of Copper and Iron After Ashing of Aqueous Solutions in Pyrex Vessels[a]

		Recovery of copper		Recovery of iron	
Vessel model	No.	Found (ppb)	% Recovery	Found (ppm)	% Recovery
A	1	24.02	96.1	4.74	94.8
	2	14.30	97.2	4.82	96.4
	3	24.20	96.8	5.00	100.0
	4	24.60	99.2	4.93	98.5
	5	24.60	98.4	4.98	98.4
	Average	24.38	97.54	4.90	97.84
B	1	25.00	100.00	4.93	98.6
	2	24.80	99.2	5.01	100.2
	3	23.50	94.0	4.92	98.5
	4	24.80	99.2	4.88	97.5
	5	24.10	96.4	4.90	98.0
	Average	24.44	97.76	4.93	98.56

[a]Model A is cylindrical and model B is rectangular in shape. Solutions to which were added 25 ppb and 5 ppm for copper and iron respectively.

TABLE 4

Iron and Copper Content in Crude and Refined, Bleached and Deodorized Palm Oil After Ashing in Glass Vessels

		Crude palm oil		Refined, bleached and deodorized palm oil	
Vessel model	Replicate[a]	Iron, ppm	Copper, ppb	Iron, ppm	Copper, ppb
A	1	4.47	48.23	1.20	8.31
	2	4.38	48.06	1.20	8.46
	3	4.44	48.71	1.18	8.23
	4	—	—	1.17	8.28
	Average	4.43	48.33	1.19	8.32
	RSD (%)	1.03	0.70	1.26	1.19
B	1	4.47	48.42	1.19	8.23
	2	4.48	48.80	1.20	8.35
	3	4.41	48.31	1.22	8.30
	4	—	—	1.20	8.31
	Average	4.45	48.51	1.20	8.30
	RSD (%)	0.85	0.53	1.05	0.60

[a] Analyses of one oil sample.

RESULTS AND DISCUSSION

The method for the determination of iron in palm oil as suggested by Wong et al. (10) has shown significant improvements in reproducibility compared to the standard method recommended by the AOCS (11). The relative standard deviation (RSD) by the former method was 0.85% compared to 2.87% by the latter method (Table 1). This difference could be due to the difficulty in controlling the flame and the use of high temperatures in the furnace used in the AOCS method. In terms of the time, the standard AOCS method takes a total of about two hr. In this respect it is more favorable than the the method (b) involving ashing in the furnace only, which takes a total of about five hr. The ashing method (c) still involves flaming before ashing. The flame was smothered periodically in order to avoid sample contamination and severe metal loss during the continuous flaming process. Overall time required for this method is about three hr., which is less than the method (b) of ashing in the furnace only. As shown in Table 1, the reproducibility (RSD) was better than by the standard method even though it is still not as good as Fung's method.

The variability was considerably greater (Table 2) for the determination of copper either because of the much lower levels of copper in the oil samples or the method of analysis itself. Results obtained by the AOCS ashing method had the greatest variability. By ashing in the furnace only, the RSD was greatly improved. When the ashing method involved flaming, smothering and ashing, the reproducibility was similar to but not better than the method involving furnace ashing only. Even though the furnace-ashing-only technique yields good reproducibility at these low levels of copper, several workers prefer flaming of the oil first before further ashing in the furnace because it is faster.

Recommended procedure. In view of this reproducibility problem with copper, an apparatus has been developed that requires less attention, accomplishes ashing faster, and yields more accurate results. The glass vessels used are cylindrical or rectangular in shape and are effective at temperatures up to 700°C. These pyrex glass vessels are relatively cheap, are easy to construct, and most importantly can withstand the ashing temperatures.

The approximately 98% (Table 3) recoveries of iron and copper from the ashing technique using these vessels were very encouraging. The high recovery probably was due to the semi-closed system used during ashing because the openings are located on the sides while the top part acts as a cover. No significant difference in recovery was observed between rectangular and round vessels. The system eliminates sputtering during ashing and is readily adaptable to a refluxing apparatus.

These glass vessels were tested with both refined, bleached and deodorized (RBD) and crude palm oil for the determination of iron and copper. As shown in Table 4, the reproducibility is much better than when other methods of ashing were used. The RSD for the determination of copper was reduced from 8.4 to about 0.5%.

The other advantage of the use of the vessel is the increased metal concentration of the final solution. In terms of sensitivity this technique can be superior to the direct injection of the oil into the atomic absorption instrument after dilution with solvent when the metals occur at ultra-trace levels.

The recommended method developed here can be extended to any application requiring ashing prior to the analysis of the metals.

ACKNOWLEDGMENTS

This work was supported by a Short Term Research Grant, Universiti Sains Malaysia.

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[Received October 20, 1987;
accepted April 28, 1988]