Comparison of Three Atomic Absorption Techniques for Determining Metals in Soybean Oil

L.T. BLACK, Northern Regional Research Laboratory,[1] Peoria, Illinois 61604

ABSTRACT

Three different atomic absorption techniques were used to analyze metals contained in three different crude soybean oils. In the first, oil was decomposed by charring followed by high-temperature dry ashing. The ash then was dissolved in a dilute acidic aqueous medium. In the second, oil diluted with methyl isobutyl ketone as the solvent was aspirated directly. In the third, the original oil sample was ashed and the metal atomized in a sequential process by a carbon rod furnace. This third technique required only μliter quantities of an oil. The analysis for many metals was similar regardless of the technique. However, values obtained for zinc, cadmium, chromium, lead, and calcium were extremely dependent upon the technique used.

INTRODUCTION

The determination of metals in vegetable oils has been under investigation for several years and is still a formidable problem. A variety of methods of analysis (1-7), including atomic absorption spectrophotometry (AAS) (2-3,7), has been published in the literature. AAS has gained acceptance in these determinations because of easy sample preparation and its analytical accuracy. Some other methods include a preparatory preconcentration step to get the metals into an aqueous matrix. Several workers (6,8-9) use charring and high-temperature (600 C) ashing (char ashing which requires 100-200 g original sample) followed by water and acid dissolution. This technique may yield low results owing to volatization of some specific metals; however, Thiers (9) found that loss of most metals can be prevented under proper ashing conditions.

List, et al., (10) reported success with a low-temperature asher, an apparatus in which oxygen plasma is generated in a radio frequency field under high vacuum also followed by water and acid dissolution; however, only 3 g can be ashed at a time. Garcia, et al., (11) reported a wet ashing procedure using nitric acid, but again all that can be ashed in a reasonable time are similar small quantities of oil. Solvent extraction or chelation has been used (12-13); however, extraction methods may be dubious especially if a large number of repetitive extractions are required. The direct aspiration of a soybean oil diluted with methyl isobutyl ketone (MIBK) has proved successful with flame AAS (14). The major drawback encountered with this technique is the dilution factor which reduces the metal content/unit volume. One of the newest AAS techniques is the carbon rod atomizer reported by Amos (15).

TABLE I

Background Metal Contents of Base Salad-Grade Soybean Oil

Metal	μg/g[a]	Percent RSD[b]
Cadmium	0.020	109
Calcium	0.033	18.1
Chromium	0.015	78
Copper	0.0067	15.1
Iron	0.082	50.1
Lead	0.012	38.5
Magnesium	0.040	5.5
Manganese	0.0065	79.3
Nickel	0.087	46.4
Potassium	<0.01	--
Sodium	0.043	32.3
Zinc	0.0042	29.4

[a] Average of four determinations as determined by char ashing and flame atomic absorption at 15 X scale expansion.

[b] RSD = relative standard deviation.

My study compares metal contents of crude soybean oil by (A) char ashing, (B) by direct aspiration of oil diluted with MIBK, and (C) by the carbon rod atomizer. Each technique has distinct advantages and disadvantages depending upon the specific metal under investigation and its concentration in the oil. The metals studied in selected soybean oils were: cadmium (Cd), calcium (Ca), chromium (Cr), copper (Cu), iron (Fe), lead (Pb), magnesium (Mg), manganese (Mn), nickel (Ni), potassium (K), sodium (Na), and zinc (Zn).

EXPERIMENTAL PROCEDURES

The AAS used in collecting these data was a Varian model AA-120 equipped with logarithmic signal output and variable scale expansion capabilities to 15 X expansion with a single slot laminar flow burner. The unit is equipped with a componental model CR-61 carbon rod atomizer, which will accept either the mini-Massmann or West-type carbon rod. The carbon rod was sheathed in nitrogen during the different heating stages to prevent premature oxidation of the rod. Under the conditions selected, the carbon rod is capable of attaining temperatures up to 3000 C. Three discrete heating stages, which are instrumentally controlled, included: evaporating the sample, ashing the sample, followed by atomizing the metals.

The crude soybean oils came from three commercial sources: (A) Illinois, 1968 crop year; (B) Arkansas, 1970 crop year; and (C) South Carolina, 1971 crop year. The last oil originated from field-damaged beans. These oils were shipped in 1 gal metal cans.

PROCEDURES

In accordance with the method of Evans, et al., (8) for char ashing, 200 g each oil was weighed into 350 ml nonetched Vycor dishes. Char ashing requires 2 days to prepare a sample; the ash then is dissolved in dilute hydrochloric acid.

Direct aspiration was accomplished by diluting 10 g oil with 40 g redistilled MIBK as reported by List, et al. (14). The metals to be analyzed were divided into sets of four. Each set of metals was prepared individually, with all four metals being determined on the same day.

The carbon rod analyses were carried out as follows: 1 μliter original oil sample was taken up in a 10 μliter Hamilton syringe previously cleaned with 5% nitric acid solution. After the sample was placed in the rod orifice, the programed power supplied a low current to dry the oil, then automatically increased it sufficiently to ash the oil, and finally raised the ash to a level sufficient to cause atomization. The absorption signal derived during the atomization level is of short duration (0.5 sec). This signal coincides with the time of maximum atom population in the rod, and the results are recorded as a peak on a strip chart recorder.

---

[1] ARS, USDA.

TABLE II

Metal Analysis of Three Different Crude Soybean Oils by Three Different Techniques

Metal	Resonance line, nm	μg/g (As is basis)								
		Char ash[a]			Direct aspiration			Carbon rod		
		Ill.	Ark.	S.C.	Ill	Ark.	S.C.	Ill.	Ark.	S.C.
Cadmium	228.8	0.0045	0.014	0.0067	0.021	0.020	0.024	0.039	0.112	0.051
Nickel	232.0	0.048	0.039	0.016	BDL[b]	BDL	BDL	0.052	0.047	0.046
Copper	324.8	0.051	0.040	0.102	0.037	0.027	0.087	0.047	0.026	0.069
Chromium	357.9	0.059	0.070	0.102	0.029	0.026	0.031	0.018	0.011	0.022
Lead	217.0	0.27	0.19	0.34	0.13	0.012	0.13	0.26	0.13	0.36
Manganese	279.5	0.30	0.64	0.64	0.27	0.73	0.63	0.31	0.83	0.76
Sodium	589.0	1.51	1.90	1.19	1.33	1.92	0.96	1.17	1.35	0.88
Zinc	213.9	1.27	1.64	2.53	1.47	1.92	2.82	1.80	1.97	2.92
Iron	248.3	1.78	1.57	6.54	1.73	1.63	6.68	1.78	1.62	6.61
Calcium	422.7	9.1	10.0	11.4	19.2	20.5	21.2	27.5	31.4	28.7
Magnesium	202.5	44.3	47.0	49.7	45.0	47.5	49.5	40.0	46.3	40.1
Potassium	404.4	157	149	255	177	174	255	144	130	226

[a] Average of two observations.

[b] BDL = below detection limit.

STANDARDIZATION

Both direct aspiration and carbon rod atomization required standards of closely matched matrices. Standards were made by dissolving the appropriate organometallic chelates in refined salad-grade soybean oil. These organometallic salts were the cyclohexane butyrates, except for tris(1-phenyl-1,3-butanediono)iron and bis (1-phenyl-1,3-butanediono)copper. These fat-soluble chelates (National Bureau of Standards) were dissolved in a combination of xylene, 2-ethylhexanoic acid, and 6-methyl-2,4-heptanedione and added directly to a salad-grade soybean oil. The standards were prepared to 500 μg metal/g and diluted to acceptable working levels. Because salad-grade oils are quite low in trace metals, they served as base oils; however, blank metal values had to be considered since some metals were present. Metal concentrations in a base oil were determined by char ashing quadruplicate samples; ash was dissolved in a mixture of 10-1 doubly distilled water and high purity hydrochloric acid. A reagent blank was prepared simultaneously. Aqueous solutions were transferred from the Vycor dishes to volumetric flasks, made to volume, and finally transferred to polypropylene bottles for subsequent AAS analyses (Table I).

Background levels of metals in the salad oil were established by the method of char ashing, and the less desirable task of preparing 12 individual method of additions curves was obviated. The concentration of each background metal so established in the oil then was added to the metal values obtained from the direct aspiration and the carbon rod techniques.

RESULTS AND DISCUSSION

To determine metals in oils, it is essential that a method be chosen in which a matched sample and a standard matrix can be prepared without the loss of any metal. Of the three methods chosen, dry ashing was the most direct approach and presented the greatest challenge. The following disadvantages added a degree of difficulty to the char-ashing technique: (A) possible metal contamination from reagents and glassware; (B) volatility of specific metals; and (C) tedious, slow operation. However, distinct advantages of dry ashing do exist: (A) under specified conditions, it gives accurate results for several metals (8-9); (B) the results obtained for each metal are absolute and need have no correction for naturally occurring metals added, as it required with the methods of direct aspiration and carbon rod; and (C) it eliminates the laborious task of establishing background metal levels by the indirect method of additions.

The direct aspiration technique also has several disadvantages: (A) standard in a base oil of known metal content must be prepared, (B) there is a possible lack of disassociation between the metal and its organic anion, and (C) particles of metal larger than 10 μ may pass through the flame undetected (16). Advantages are: (A) rapidity, (B) little chance of positive contamination, and (C) increased sensitivity as a result of signal enhancement by ketone matrices. The third method selected for comparative study as the newer technique of carbon rod atomization. Its disadvantages are: (A) slightly less precision than flame AAS, (B) high initial expense, and (C) high degree of technical ability required. Carbon rod atomization has an impressive list of advantages: (A) small samples (1 μliter); (B) rapidity (60-80 samples/hr); (C) high degree of sensitivity due to a long exposure time to the resonance line (0.5 sec), i.e. a greater number of atoms reaching ground state and little chemical or emission interferences; and (D) no sample pretreatment.

The possibility of interference from nonatomic absorption was checked with a hydrogen continuum lamp; however, this effect was negligible, regardless of technique.

SAMPLE RESULTS

The values, expressed as μg/g, for each metal (listed in increasing order of concentration) in the three crude soybean oils analyzed by each method are shown in Table II. For most elements, the primary resonance line was used; however, because of their high concentration, Mg and K were determined at a secondary line. Values were obtained for all metals, except for those Ni analyses by direct aspiration where the dilution effect caused too large a drop in sensitivity.

Least significant ratio (LSR) and percentage relative standard deviation (RSD) to the geometric mean appear in Table III for three different oils, as determined by the three different methods. When the ratios of any two values exceed the LSR, there is a significant difference between techniques, whereas variability between oils is reflected in the percentage RSD.

Some conditions that may affect the apparent precision are listed in Table IV. Losses because of the volatility of Zn and Cd have been reported (9,17). Char ashing may yield low results for these elements, especially if the ashing is carried out for sustained periods at high temperatures. Also during the ashing cycle of the carbon rod, similar losses may occur if the ashing temperature is too high even briefly. Besides volatilization, char ashing done in the open air can easily result in contamination, especially with the more ubiquitous elements, such as Na and Pb.

As might be expected, solvent dilution of the oil required in direct aspiration greatly reduces the effective sen-

TABLE III

Geometric Mean of Three Different Oils by Three Different Techniques

Metal	μg/g Char ash	μg/g Direct aspiration	μg/g Carbon rod	LSR[a]	RSD, %[b]
Cadmium	0.0075	0.0216	0.0606	2.23	43
Nickel	0.0311	--	0.0483	2.36	46
Copper	0.0593	0.0443	0.0439	1.39	14
Chromium	0.0750	0.0286	0.0163	1.57	22
Lead	0.259	0.0594	0.230	3.86	81
Manganese	0.494	0.499	0.580	1.16	6.7
Sodium	1.51	1.35	1.12	1.20	7.9
Zinc	1.74	1.20	2.18	1.15	6.3
Iron	2.63	2.66	2.67	1.05	1.8
Calcium	10.1	20.3	29.2	1.15	6.3
Magnesium	47.0	47.3	42.0	1.14	5.7
Potassium	181	199	162	1.12	5.1

[a] LSR = least significant ratio.

[b] Calculated from a two way analysis of variance.

TABLE IV

Conditions That Affect Method Precision

Metal	Char ashing	Direct aspiration	Carbon rod
Cadmium	Volatility	Solvent dilution	
Nickel		Solvent dilution	Incomplete atomization
Copper			
Chromium		Solvent dilution	Incomplete atomization Oxidation state
Lead	Contamination	Solvent dilution	
Manganese	Phosphorus interface	Phosphorus interface	
Sodium	Contamination CaOH emission	Contamination CaOH emission	Contamination
Zinc	Volatility		
Iron			Incomplete atomization
Calcium	Flame and chemical interfaces	Cool flame and solvent interfaces	
Magnesium			Too sensitive—at weakest resonance line
Potassium	Ionization	Ionization	Ionization

sitivity and makes it difficult to determine the elements that are present in ng quantities. Of the metals with high vapor pressures, Fe, Ni, and Cr are not atomized completely on the carbon rod. Consequently, the carbon rod assembly must be cycled through the different heating stages with no sample to remove any remaining traces of metal. Signal depression due to the ionization of K is an important factor and may have influenced the results between methods for K in this comparative study. The element that is most difficult to determine accurately is Ca. The presence of organic solvents affects the position of maximum absorbance in the flame. In addition, cooler flames interfere with Ca determination by AAS, such as the formation of stable oxysalts with high concentrations of phosphorus. The need for a releasing agent, such as lanthanum or strontium, is mandatory. The disparity in Ca results (Table II) probably can be accounted for from the following facts: crude soybean oil contains high quantities of phosphorus; however, neither the aqueous solution from char ash nor the solvent aspiration solution contained a releasing agent.

In the carbon rod atomizer, the absorbance of Cr depends upon the oxidative state, which affects decomposition kinetics. Preferably, all the Cr should be in the hexavalent state. The low values for Cr by the carbon rod method might be attributable to its oxidation state.

Within the framework of conditions set forth in this comparison, the following conclusions may be drawn: Cu, Fe, Mn, or Na may be run with equal success by any of the three methods reported. Mg and K can probably also be run with equal success; however, the concentration of these two metals in crude soybean oil is too great for successful use of the carbon rod atomizer as a reliable technique. Cd is definitely lost by char ashing, with the possibility that some Zn also may be lost. Cd, Ni, and Pb are all adversely affected by sensitivity limits when the direct aspiration technique is followed. The use of direct aspiration or carbon rod appeared to be unsuccessful for Cr, owing to the oxidative state which it must be in for successful AAS. Ca was run most successfully by carbon rod atomization and with less success by the other two methods, because a releasing agent was missing; such an agent is mandatory for both char ashing and direct aspiration.

ACKNOWLEDGMENTS

Statistical analyses were provided by W.F. Kwolek, biometrician, North Central Region, U.S.D.A., stationed at the Northern Laboratory.

REFERENCES

1. Abbott, D.C., and R.D.A. Polhill, Analyst 79:547 (1954).
2. English, M., and D.C. Manning, At. Absorption Newslett. 3:65 (1970).
3. Guglillaumin, R., Ibid. 5:19 (1966).
4. Høgelahl, O.T., and S. Melsom, Anal. Chem. 38:1414 (1966).
5. Labuza, T.P., and M. Karel, J. Food Sci. 32:572 (1967).
6. Meliun, E.H., and J.E. Hawley, JAOCS 28:346 (1951).
7. Piccolo, B., and R.T. O'Connor, Ibid. 45:789 (1968).
8. Evans, C.D., G.R. List, and L.T. Black, Ibid. 48:840 (1971).
9. Thiers, R.E., in "Methods of Biochemical Analysis," Vol. 5, "Contamination in Trace Element Analysis and Its Control," Edited by David Glick, Interscience Publishers, New York, N.Y., 1957.
10. List, G.R., R.L. Hoffmann, W.F. Kwolek, and C.D. Evans, JAOCS 45:872 (1968).

11. Garcia, W.J., C.W. Blessin, and G.E. Inglett, Cereal Chem. 49:158 (1972).
12. Prevot, A., At. Absorption Newslett. 5:13 (1966).
13. Price, W.J., J.T.H. Roos, and A.F. Clay, Analyst 95:760 (1970).
14. List, G.R., C.D. Evans, and W.F. Kwolek, JAOCS 48:438 (1971).
15. Amos, M.D., Amer. Lab. 2:33 (1970).
16. Bartels, T.T., and M.R. Slater, At. Absorption Newslett. 9:75 (1970).
17. Garcia, W.J., C.W. Blessin, an G.E. Inglett, Cereal Chem. 51:788 (1974).

[Received November 18, 1974]