Atomic Absorption Spectroscopy[1]

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Abstract

Atomic absorption spectrophotometry has been used for the rapid determination of various metallic and nonmetallic elements in crude and refined vegetable oils and in animal fats, many present in levels of parts per million. Various types of crude and refined vegetable oils were analyzed for Ca, Cu, Fe, Mg, Mn, P and Zn. This method of analysis has proven to be less time consuming, as accurate and more convenient than other spectroscopic techniques for elemental analyses.

Introduction

SINCE WALSH (1) AND RUSSELL ET AL. (2) first suggested the use of atomic absorption spectrometry for analytical purposes, it has found ever increasing application in the analysis for trace elements in a very large number of materials. Atomic absorption techniques have been developed for determining the trace amounts of trace elements in biological fluids, industrial products, alloys and agricultural products. An agricultural product which seems to be amenable to analysis by this technique is the oil extracted from certain plant seeds such as cottonseed, soybean, peanut and safflower oils.

Until recently, there has been relatively little interest in the trace element content of these oils, except for some concern regarding the role of specific trace metals in promoting or accelerating rancidity (oxidation). However, expanded use in the manufacture of solid shortenings where metals such as nickel are used as catalyst has increased interest in the development of a technique to determine these elements in trace quantities. Similarly increased awareness of the correlation between Cu, Fe (and probably other metals) content of the oils, and the color stability of the fully refined oil requires additional attention to the role of trace metals in the deterioration of stored oils.

To date there have been very few analytical procedures for the determination of trace elements in oils and these procedures have been both difficult and time-consuming. The analytical techniques for elemental analysis usually involved wet chemical procedures such as iodometric titration for bromine (3), Parr oxygen bomb method for chlorine (4) or other similar techniques for calcium and phosphorus. The only analytical technique which involved the use of instrumentation was emission spectroscopy employing the spectrograph to determine the elemental composition of the oil sample (5). The drawback to this procedure is the exceedingly long and tedious sample preparation involving wet or dry ashing resulting in a lengthy total analytical technique (6).

Even with the advent of atomic absorption instrumentation and development of techniques in other areas, little research has been attempted to establish methods using this type of instrumentation as a tool for the trace elemental analysis of oilseeds. In this paper some preliminary data obtained from the analysis of several types of oils by atomic absorption spectroscopy are presented.

Experimental Methods

Atomic absorption techniques involve three requirements: a source of radiation that can be absorbed by the atoms from the sample to be analyzed, a means for converting the sample into the vapor state which will absorb radiation from a standard source of the element to be determined, and an instrument to measure the reduction in radiation produced when it is passed through the vapor consisting of partially excited atoms from the analytical sample (7). A schematic representation of this system is shown in Fig. 1.

The first requirement is fulfilled by using a hollow cathode lamp as a source of radiation. Hollow cathode lamps are available for most metals and

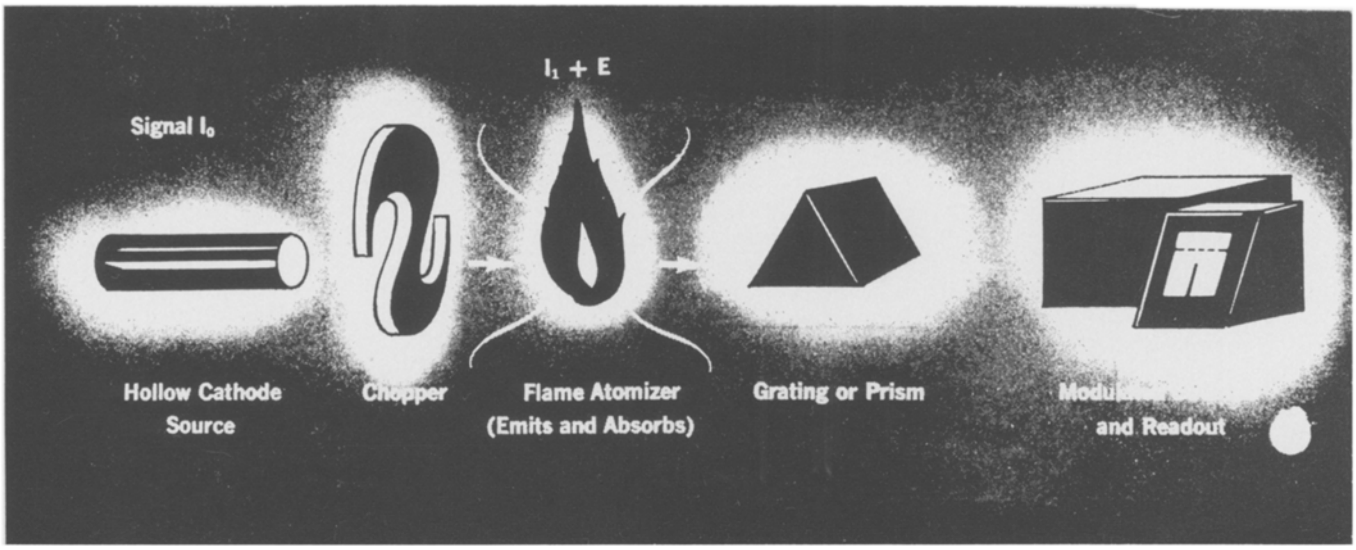

FIG. 1. Schematic representation of an atomic absorption system.

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[1] Presented at the AOCS-AACC Joint Meeting, Washington, D.C., April, 1968.
[2] So. Utiliz. Res. Dev. Div., USDA, ARS.

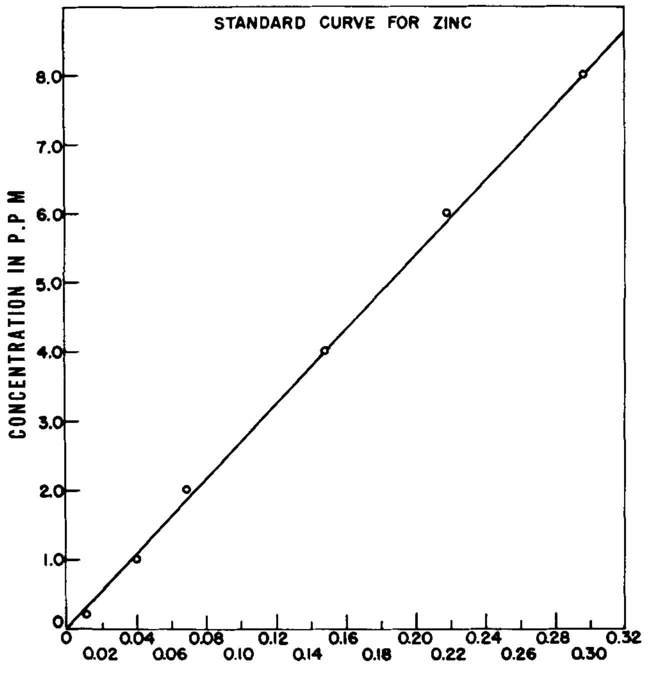

FIG. 2. Standard curve for zinc.

many nonmetals. The lamp produces the emission spectrum of a specific element when excited by an electric current. The excited atoms produce a beam which is passed across the path of an elongated burner.

The burner-atomizer is the second link required. Here the analytical sample is aspirated to form a fine mist which is burned in the oxidizer-fuel system appropriate to the analysis being performed. The oxidizer-fuel systems used are oxyacetylene, air-acetylene, nitrous oxide-acetylene, air-hydrogen and air-coal gas. Each has its own advantages and limitations. The most generally appropriate and the most widely used is the air-acetylene system.

The burning of the sample produces a population of atoms needed to absorb the radiation from the beam of the hollow-cathode lamp. The decrease produced when an analytical sample is atomized in the flame has been found to be proportional to the concentration of the element in the sample. This decrease in energy is measured as a per cent absorption and then translated into concentration by means of a calibration curve previously prepared by plotting the per cent absorption obtained by burning standards containing known concentrations of the element against the concentration. A typical standard curve for zinc is shown in Fig. 2.

In the experiments described in this paper a Perkin-Elmer atomic absorption instrument model 303, equipped with a Digital Concentration Readout Accessory (DCR-I) was used. The line sources of the emission spectrum were hollow-cathode lamps of the specific element being analyzed, operating at the specific current for which each lamp was rated. The sample was atomized and burned in a Boling Burner Head using the air-acetylene oxidizer fuel system. The results obtained were printed out on tape by the DCR-I.

Analytical Methods

A series of standards was prepared for each element to be determined by dissolving a specified amount of an appropriate organo-metallic compound, obtained from the National Bureau of Standards in 100 g of metal-free oil obtained by molecular distillation.

Dissolution of the compound was facilitated by the addition of small amounts of 2-ethylhexanoic acid and 2-ethyl-hexyl amine and heating slightly. This procedure gave a standard solution containing 500 ppm of the element under investigation. Portions of this solution were diluted with methyl-iso-butyl-ketone to give working standards within the appropriate working range usually between 1 and 2 ppm (8).

In this study we used minimal sample preparation. Ten milliliters of the analytical oil sample was diluted to 50 ml with methyl-iso-butyl-ketone. The samples analyzed were oils donated by various oilseed processing companies throughout the country. They included crude and refined safflower, soybean, cottonseed, sesame, peanut, sunflower, coconut and rapeseed oils. Some samples of solid fats, such as lard and stearine, were included but difficulty was experienced in keeping them in solution and occasionally the capillary became clogged while the sample was being aspirated.

In the analytical procedure the instrument was first zeroed by burning the methyl-isobutylketone solvent used. The digital concentration accessory was then set at the range of concentration the sample was suspected of containing by burning a standard of the appropriate concentration. These two steps were repeated until the concentration readout corresponded to the concentration of the standard. The accuracy was checked by introducing another standard of known concentration and checking to establish that this concentration was printed out by the digital concentration readout.

After the digital concentration readout had been calibrated the samples were run one after the other with the standard being interspersed after every five or six samples to ascertain that no changes were occurring in the calibration. The concentration of the element in question was printed out in parts per million on tape, each printout being the average of four readings. Two, and sometimes three, printouts per element were obtained for each analysis. Each final result was the average of from 8 to 12 instrumental readings.

Results

Twenty-one samples of vegetable oils were analyzed for sodium, calcium, manganese, copper, iron and zinc. We had planned to include magnesium and nickel in the analysis but difficulty has been encountered in obtaining oil-soluble compounds for standards. This problem is part of continuing evaluation of atomic absorption analyses underway at our laboratory.

Results of our analyses showed considerable varia-

TABLE I

Trace Metal Content of Vegetable Oils

Oil	Condition of Sample	Concentration in ppm of				
		Sodium	Calcium	Copper	Iron	Zinc
Sunflower	Crude	8.45	13.6	0.20	1.40	1.75
Rapeseed	Refined & Bleached	4.65	1.0	0.15	0.55	1.15
Corn	Refined	6.45	0.3	0.10	0.60	1.00
Peanut	Unknown	4.10	26.9	ND[a]	1.85	2.10
Peanut	Unknown	5.70	19.5	ND[a]	1.75	1.65

[a] ND indicates not detected.

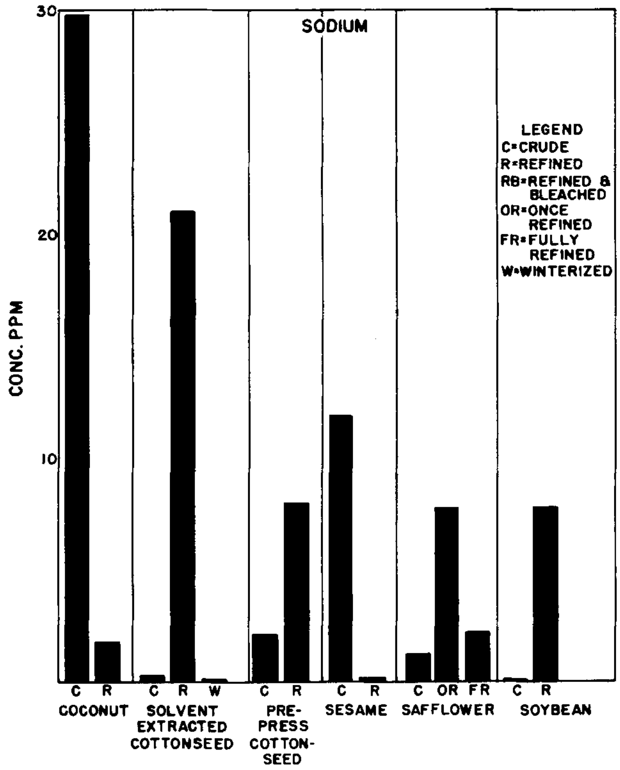

FIG. 3. Sodium content of crude and refined vegetable oils.

tion in trace element content among various types of vegetable oils tested and also, as could be expected, between the crude and refined samples of the same types of oils. Table I shows the concentration in parts per million of sodium, calcium, copper, iron and zinc. These oils were either the crude or the refined samples—both were not available for analyses of the same oil. No information as to the processing of the peanut oils was available.

Fig. 3 shows a comparison of the sodium content of various crude and refined vegetable oils. The coconut and sesame oils show a marked reduction in sodium content in the refined sample in comparison to the crude sample. In the cottonseed and soybean oils this result is reversed with an increase in sodium being noted in the refined sample, probably arising from incomplete removal of the sodium soaps formed during the alkali refining.

Figure 4 shows a comparison of the iron content of the same series of oils. As can be noted, the range of concentration is not as varied as it was for sodium. The concentration was not very high, iron being present as a trace metal ranging in the crude oils up to about 1.5 ppm. The decrease in the refined sample was not very great especially in the case of the cottonseed oils. There was a decrease of approximately 50% in sesame, coconut and soybean oils and a decrease of only 0.25 ppm for the cottonseed and safflower oils. This persistence of iron content in cottonseed oil may be a factor in color stability of oil in storage.

Figure 5 continues the comparison of these oils with the concentration of calcium. In this case the reduction in the amount of calcium during refining was quite dramatic. In two of the oils the calcium content was not detectable in the refined sample. The range of concentration for colcium in the crude oil samples vary widely from a low of approximately 0.3 ppm in a crude safflower oil to a high of approximately 34.0 ppm in the crude sesame oil. The cottonseed oil samples again showed a persistence of calcium even in refined oil samples.

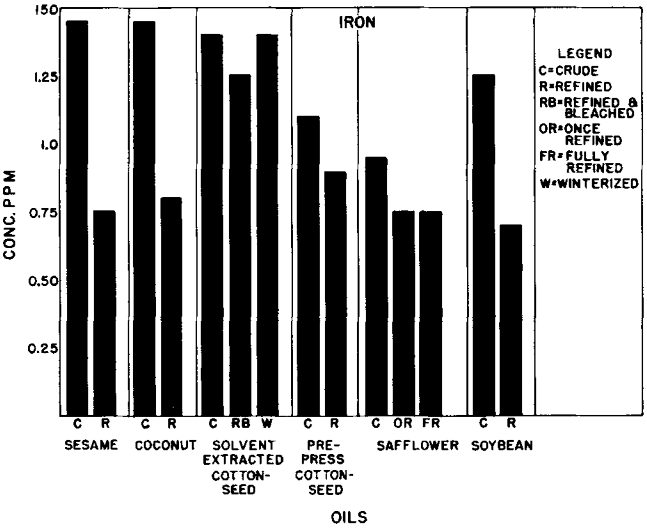

FIG. 4. Iron content of crude and refined vegetable oils.

Figure 6 shows the comparison of the concentration of zinc in the same oil samples shown in the preceding figures. The highest concentration was 9.3 ppm in sesame crude oil and a low concentration of approximately 1 ppm was found in crude cottonseed oil. The low zinc concentration occurred in both crude and refined cottonseed oils.

The level of concentration of copper and manganese was low and almost constant in all samples analyzed ranging approximately 1.5 ppm for manganese and approximately 0.15 ppm for copper in about half the samples. The other samples had a concentration of copper too low to be detected.

An attempt was made to correlate these results by analyzing some of the oils by x-ray fluorescence

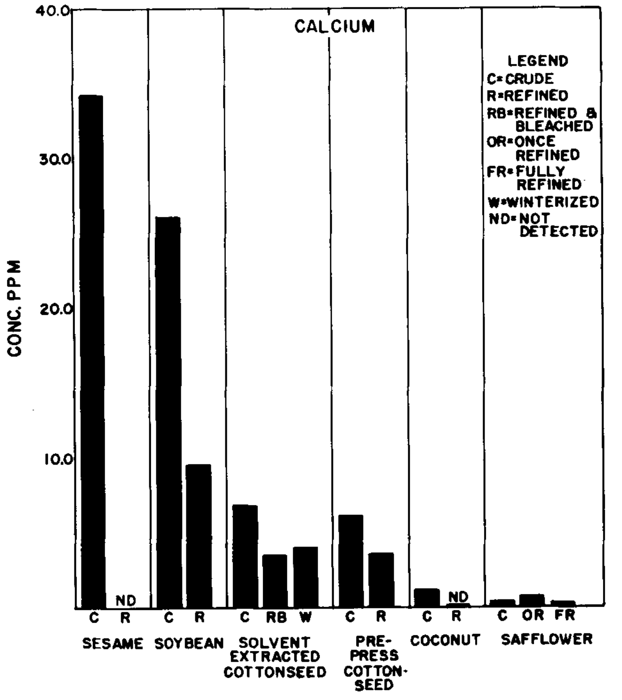

FIG. 5. Calcium content of crude and refined vegetable oils.

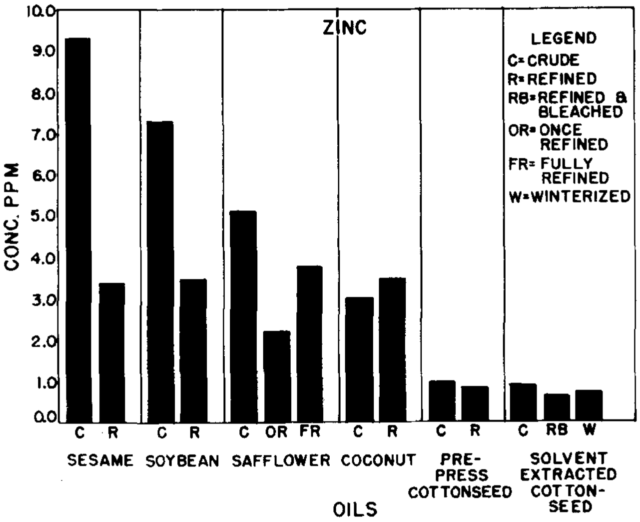

FIG. 6. Zinc content of crude and refined vegetable oils.

spectrometry (9) but, except for a few of the samples having extremely high calcium content, the concentrations were too low to be analyzed by this method.

Tables II and III demonstrate the results obtained when known amounts of calcium and zinc were added to samples of oil containing varying concentrations of these two metals.

A sufficient amount of calcium standard solution was added to samples of rapeseed, sesame and peanut oils to increase the concentration of metal by 1 ppm in the rapeseed and peanut oil samples, and 10 ppm in the sesame oil samples. The results show a difference of only 0.4 to 0.2 ppm between the calculated and observed results.

To samples of rapeseed, corn and peanut oils sufficient zinc standard solution was added to increase the zinc concentration of these samples by 1 ppm. In these analyses the difference between the theoretical yield and the observed yield was only 0.5 to 0.2 ppm. Similar experiments are planned for the other metals in these oils.

TABLE II
Recovery of Calcium Added to Oils

Oil	Calcium in oil ppm	Calcium added ppm	Calcium content calculated	Found ppm
Rapeseed oil	1.00	1.00	2.00	2.23
Sesame oil	34.2	10.00	44.20	44.40
Peanut oil	26.9	1.00	27.90	27.94

TABLE III
Recovery of Zinc Added to Oils

Oil	Zinc in sample ppm	Zinc added ppm	Zinc content calculated ppm	Zinc content found ppm
Rapeseed oil	1.15	1.00	2.15	2.27
Corn oil	1.00	1.00	2.00	2.25
Peanut oil	2.10	1.00	3.10	3.15

Discussion

The preliminary results reported in this paper indicate that the trace metal analysis of vegetable oils is feasible by means of atomic absorption spectroscopy. Although direct dilution of the oil by means of a solvent and its analysis seems to be adequate, other means of sample preparation, such as ashing the oil and taking up the residue in 0.2 N HCl and analyzing this solution will be tested.

Additional studies must be completed before a method for trace element analysis of oils by atomic absorption spectroscopy can be finalized. These results, however, show that such a method can be developed and that it compares quite favorably with other methods of analysis in simplicity, speed and reproducibility.

ACKNOWLEDGMENT

N. H. Kuhrt, of Distillation Products Industry, provided samples of molecularly distilled oil; Anderson Clayton, Pacific Vegetable Oil Corp., Swift and Co., and Ranchers Cotton Oil Co. provided samples of oils.

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