Direct Determination of Sodium in Soybean Oil by Flame Photometry[1]

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Abstract

The correlation of sodium content of alkali-refined soybean oil with the soap content of the oil has been widely accepted by oil processors. We have found that this sodium content can be determined by aspiration of an oil solvent solution directly into a flame emission spectrophotometer. The intensity of the sodium flame emission produced from the oil solution was compared with that from oil standards containing known amounts of sodium soaps. To prepare standards, sodium oleate was dissolved in ethylene glycol followed by the addition of a solvent and soybean oil containing low sodium of known amount; this solution aspirated at a rapid, constant rate. The method is capable of determining sodium at a lower limit of 0.1 ppm with accuracy comparable to that of neutron activation analysis.

Introduction

A high-quality alkali (sodium hydroxide)-refined soybean oil intended for edible uses should have a low soap content, usually from 5 to 10 ppm (1). Since the general belief is that essentially all soap in soybean oil is in sodium form, determining the amount of sodium should give a good measure of soap content (2). During studies on sodium removal from alkali-refined soybean oil by a continuous water-wash, ion-exchange technique (3), a quick, accurate measure of sodium level was required. Several quantitative analyses for soap have been reported in the literature. Among these are ashing (4), extraction (5–7), direct titration (8), ion exchange (9) and electrical conductivity (10). Atomic absorption (11) and neutron activation (12) are useful for determining sodium which data can be related to soap content. Neither speed, sensitivity nor accuracy is common to any one method with the possible exception of atomic absorption and neutron activation; however, equipment for these two methods is quite costly.

Flame emission spectrophotometry has been applied in many diverse determinations of alkali metals (13,14). Edmonds and Mattikow (2) measured sodium soaps by flame photometry emission of sodium in a water extract of vegetable oils. While their procedure has good sensitivity and accuracy, it is relatively slow and laborious compared to the method described in this paper based on direct aspiration of a soybean oil solvent into a flame photometer. The intensity of the sodium flame emission from the sample is compared with that from oil solvent standards of known soap content. Oil samples can be analyzed in a few minutes with good accuracy, precision and sensitivity.

Analytical Procedures

To prepare a sample for analysis, 2.00 g of an oil was weighed into a 10 ml volumetric flask that had been rinsed five times with distilled water and dried. Three tenths of a gram of ethylene glycol was added to the oil. The mixture was warmed gently for a few seconds on a hot plate to dissolve any undissolved soap, then cooled and made up to volume with methyl ethyl ketone (MEK). Standard samples were prepared as follows: 132.4 mg of sodium oleate, weighed into a 500 ml volumetric flask, was dissolved in 15.0 g ethylene glycol by warming on a hot plate. Soybean oil (100.0 g) containing a known low amount of sodium was added to the flask and MEK was added to volume. This standard solution contains 1324 ppm sodium oleate per gram of soybean oil (100 ppm sodium per gram). Standards at other levels were prepared by the same procedure, but the amount of sodium oleate varied. Low sodium soybean oil, from which the standard sodium oleate samples were made, was prepared by washing refined, bleached oil 10 times with distilled water. The remaining sodium in the washed soybean oil was subsequently measured by adding known amounts of sodium oleate to several samples of the washed oil and then determining luminosity values in arbitrary units (% T) by aspiration into the flame photometer. The luminosity value was plotted against the known sodium content for each sample. Extrapolation provided the sodium content of the washed oil (Fig. 1).

Samples and standards were analyzed on a Beckman DU-2 spectrophotometer equipped with a flame emission accessory. The operating conditions selected were as follows: Gas pressures at the control panel were oxygen 20 psi and hydrogen (fuel) 4 psi. Flow rate of the fuel was regulated to center the flame in the optical path of the detector. A wavelength of 589.3 mμ was slightly adjusted for maximum energy yields from the sodium flame. The slit width controlled the meter needle (range). Other settings were: phototube-blue, load resistor-photomultiplier, sensitivity-7, per cent transmission (T) scale expanded to 0–10% full scale. The burner was allowed to equilibrate for 3 min after ignition.

A standard curve was prepared by selecting one

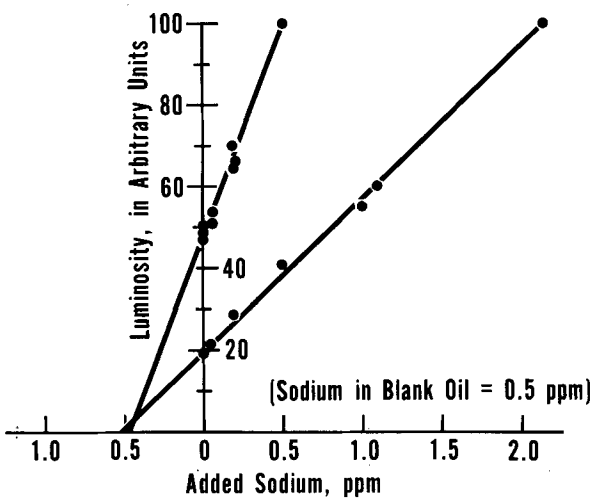

FIG. 1. Determination of sodium in soybean oil used to prepare standards (based on two different sensitivity settings).

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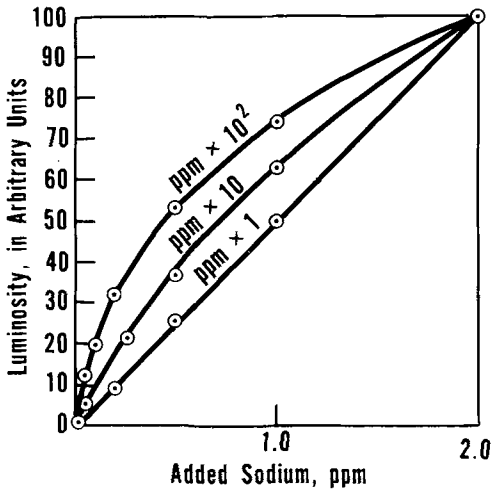

FIG. 2. Sodium standardization curves. (Standard oil contained essentially no sodium.)

of the standard mixtures containing sodium closest to the maximum expected among the samples. This selection was made after a trial comparison between standards and a few random samples. When a standard sample was chosen which would not be exceeded in sodium content by any of the samples to be analyzed, the slit width was adjusted with that standard to read 100% T. Standards containing less sodium were used to complete the standard curve (Fig. 2). The standard curve was drawn by plotting the concentration of sodium as the abscissa against the luminosity values as the ordinate. The concentration of sodium in the unknown sample was determined by reading its flame luminosity and determining sodium from the standard curve.

Standard solutions were aspirated first, followed by the unknown samples. After every two to three samples, burner stability was checked against the maximum standard chosen.

Results and Discussion

The high viscosity of soybean oil and the limited solubility of its soaps in the oil are two major objections to determining sodium by direct aspiration of the oil into a flame photometer. Undissolved soaps are frequently found mixed with oil after alkali-refining operations.

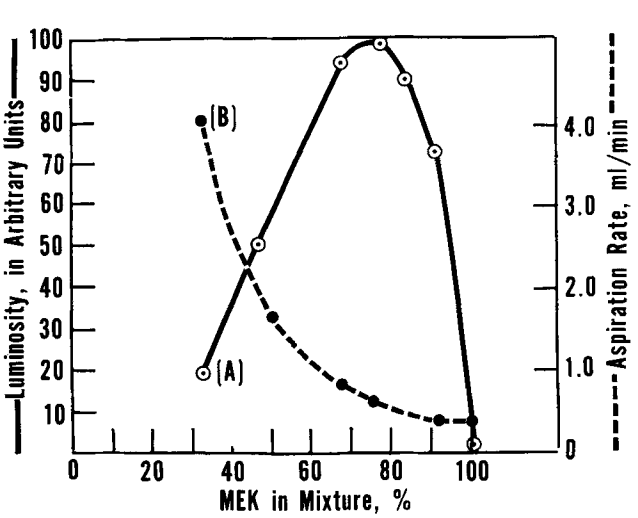

FIG. 3. Relationships between (A) viscosity vs. luminosity; (B) effect of methyl ethyl ketone-oil mixture on oil aspiration rate.

TABLE I

Sodium Determination by Direct Photometry; Precision

Sodium content of soybean oil, ppm					Relative standard deviation, %
Day					
1st	2nd	3rd	4th	5th	
0.09	0.08	0.08	0.11	0.06	±21.6
0.35	0.43	0.47	0.45	0.40	11.2
1.07	1.13	1.10	1.14	1.09	7.3
2.45	2.41	2.53	2.68	2.65	4.7
6.4	6.8	6.8	6.2	6.2	4.7
15.9	15.9	15.9	15.2	15.2	2.5
35.4	33.7	32.6	31.8	34.5	6.2
81.1	82.4	82.4	84.2	84.2	1.6

The high viscosity of soybean oil causes it to aspirate at a slow and irregular rate. Adding solvent to the oil serves two purposes. The solvent dilutes the oil and decreases its viscosity, and the aspiration rate increases sufficiently to increase the net rate of oil being introduced into the burner. In addition, certain organic solvents enhance the emission spectra of alkali metals because the added solvent forms radicals that either act by direct excitation or prevent interference of other radicals (15). MEK was selected as the dilution solvent since it exhibited both these characteristics and was also readily available. Other ketones, such as methyl isobutyl ketone, were tried with similar results. The optimum ratio of MEK to oil (Fig. 3) was determined by aspirating a series of MEK-oil mixtures of known proportions. The maximum sodium emission occurred at approximately the 80% MEK level (four parts MEK to one part oil). Beyond this percentage of MEK the oil solution became too dilute, resulting in reduced sodium emission.

Because sodium soaps were not soluble with the oil solvent mixture chosen, the soap was dissolved by adding ethylene glycol before MEK was added, followed by gentle heating and thorough mixing. All components of the mixture were brought into mutual solution by the addition of MEK. This solution could be aspirated efficiently by the flame photometer.

At the optimum level of MEK aspiration the viscosity of the MEK-oil-glycol solution was close to that of water. However, aqueous sodium standards for MEK-oil-glycol samples were unsatisfactory. Since small variations in viscosity produce large differences in aspiration rate and therefore in emission, viscosities of aqueous standards and oil solutions would have to be carefully matched. Also, the enhancement of emission due to the solvent would not occur with aqueous standards. In addition, when aspirating aqueous standards, the flame requires realignment with the detector to obtain maximum luminosity since water yields a flame with a lower center of luminosity than MEK due to ignition of MEK as it leaves the burner.

Sodium emission above the level of about 3–5 ppm yielded nonproportional luminosity (Fig. 2). This effect results from the self-absorption of the light being emitted (16).

Data on the precision of the determination are presented in Table I. Eight samples with sodium concentrations ranging from 0.1 to 80 ppm were each analyzed on five different days. By the method of Edmonds and Mattikow (2) we found 1.3, 7.1 and 37 ppm sodium in three soybean oils by extraction photometry; in comparison, by direct photometry, we found 1.2, 6.5 and 34 ppm sodium in these same samples. The values are in reasonably good agreement. Because the slightly higher values obtained by extraction photometry show a consistent deviation,

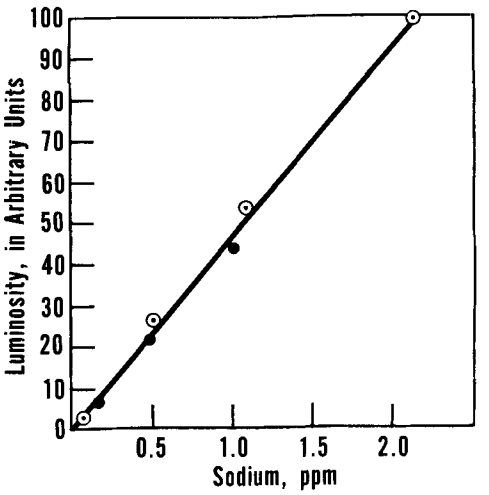

FIG. 4. Direct photometry comparison of sodium analysis: ⊙ sodium determined by flame photometry from oils previously analyzed by neutron activation; ● sodium oleate added to essentially sodium-free oil.

the difference might be attributable to variation between aqueous and solvent oil standards. The direct photometry method was standardized with the sodium oleate solvent standard as described, whereas the extraction photometry method was necessarily standardized with aqueous sodium standards.

To compare flame photometry with neutron activation, soybean oils whose sodium content had previously been determined by neutron activation were aspirated in the flame photometer. The emission intensities of these samples were plotted vs. their known sodium content and compared with a series of sodium standards run in the same manner (Fig. 4). Because both series of analyses followed the same slope, good agreement was indicated between the methods.

The flame photometry method has been applied extensively to soybean oil; however, it could probably be applied to any vegetable oil if the corresponding oil is used to make the standard solutions.

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