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Automatic Karl Fischer Titration of Moisture in Sunflower Seed[1]

JAMES A. ROBERTSON and **W.R. WINDHAM**, R.B. Russell Agricultural Research
Center, USDA, ARS, PO Box 5677, Athens, GA 30613

ABSTRACT

An automatic Karl Fischer (KF) titrator of the motor-driven buret type was applied to the determination of moisture in sunflower seed. A study of the effect of sample size on KF moisture analysis showed a significant decrease in moisture content with increase in sample size from 1 to 5 g. In the moisture range of 5.5-10.5%, a sample size of 3-4 g gave moisture values closest to those obtained by the AOCS official oven method for sunflower seed. Comparison of KF moisture analysis with oven methods on 6 samples with moisture contents ranging from 5.4 to 12.7% showed that KF moisture values were not significantly different from air oven and vacuum oven methods. The mean standard deviation of KF determinations of whole sunflower seed was 0.11% moisture content, whereas for forced draft oven moistures, the mean standard deviation was 0.05%. KF moisture values generally were slightly lower than the air oven moisture values. Using KF and vacuum oven methods to measure moisture contents, sunflower seed were found to lose 0.6% moisture from a sample containing 8.9% moisture when grinding the sample with Hyflo Super Cel as in the AOCS official method.

INTRODUCTION

In a study of the application of near infrared reflectance (NIR) spectroscopy for determining moisture in sunflower seed, a calibration method was needed to determine as accurately as possible the "true" moisture content of the seed.

The Karl Fischer reagent titration method (KF) is specific for water and has the added advantage that it is much more rapid for many materials than official oven methods (1). The KF method has been applied to a wide variety of organic materials such as butter and margarine (2), cereal and cereal products (1), ground cottonseed (3), grain (4,5) and soybean meal (6).

Fosnot and Haman (1) determined the moisture in cereals and cereal products by the KF method and reported that the two most important factors in the analyses were the length of time that the material was in contact with the Fischer reagent and the particle size of the sample. Ground cereal was placed in flasks with methanol and brought to boiling. After cooling to room temperature, the sample was titrated to excess with Fischer reagent, allowed to stand for a specified time, and then the endpoint was determined electronmetrically according to the "dead-stop" procedure using a cathode ray tube. They found a contact time of 30 min and a grind of ½ mm or less gave complete extraction of moisture. With a wide variety of cereal products ranging from 1% to 80% moisture, agreement with the oven method was in most instances very good.

Hoffpauir and Petty (3) compared oven drying with KF titration for determination of moisture in ground cottonseed products. Ground cottonseed samples were extracted with anhydrous methanol by allowing the sample to stand for 3 hr at room temperature, with frequent shaking, and then titrating directly with KF reagent. For fumed and ground cottonseed and ground cottonseed meal, moisture values by the KF method were lower than that by both vacuum and air oven at 101 C. They concluded that the lower values might be due to inadequate extraction of water with methanol or that some volatile components other than water are lost in the oven method.

Krober and Collins (6) used the KF procedure to determine the moisture content of extracted soybean meal. Soybean meal was extracted with dry methanol by allowing the sample to stand for 1 hr and then shaking it for 15 min with a mechanical shaker. The mixture was titrated directly with KF reagent to a visual endpoint. The results agreed with oven analysis within 0.1% for samples of moisture content between 1.5% and 16.8%.

Although the KF method, in the absence of interferences, is specific for water and can be used to analyze materials with volatile components and heat labile substances, the method required considerable technical skill

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and experience for accurate, reliable results (1). However, the disadvantages have been largely overcome with the development of electrometric endpoint detection, automatic dispensing of KF reagent from a buret and coulometric generation of iodine which eliminates the buret (5). As a result of these developments, two types of automatic KF titrators with electrometric endpoint detection are commercially available: titrators with motor-driven burets and titrators with coulometric generation of iodine. Jones and Brickenkamp (5) used both types of automatic KF titrators to determine the moisture content of corn, soybeans, grain sorghum, wheat, oats and rice. They eliminated the problems of moisture loss during grinding of sample and the effect of particle size by grinding the whole seed in a hardened steel vessel with steel balls using a Spex Mixer/Mill which reduces the sample to very fine particles. The automatic method was found to be precise (standard deviation typically 0.07% moisture content at a moisture content of 15%) and easy to use by personnel having little formal technical training. The primary instrument used in the study was an Aquatest II coulometric titrator; however, the amount of water that can be titrated with the titrator was found to be ca. 0.07 g/day. This severely limits the number of samples that can be analyzed by the instrument, which is also quite expensive.

In the present study, an automatic KF titrator with a motor-driven buret with no water-quantity limitation was evaluated in the KF determination of moisture in whole or ground sunflower seed.

MATERIALS AND METHODS

Apparatus

A Fisher K-F Model 392 automatic titrator with a Fisher automatic Burette/Dispenser Model 395 was used for titrations. A Spex Model 8000 Mixer/Mill (Spex Industries, Metuchen, NJ) with a hardened steel vessel of 65 mL capacity and 1.27-cm (0.5-in.) diameter steel balls were used to mill sunflower seed in methanol to extract water. Becton-Dickinson BD-6440 Vacutainer tubes (Becton-Dickinson & Co., Rutherford, NJ) were used to store methanolic extracts temporarily. A Mettler H20T analytical balance and a Sartorius 1265 MP electronic-top loading balance were used in the analyses. A 50-mL Universal repipet dispenser was used to dispense methanol from a 4-L bottle.

Reagent

Stabilized Karl Fischer reagent was used with the Fisher titrator. Baker HPLC methanol (ca. 0.004% water) and Burdick & Jackson distilled in glass methanol (ca. 0.02-0.04% water) were used to extract the water.

Sample Preparation and Extraction

The extraction of water from the sunflower seed was by the procedure of Jones and Brickenhamp (5). A sample of sunflower seed on which water determination was to be made was rapidly and accurately weighed on an analytical balance. The sample and 3 milling balls were immediately put into the milling vessel of the mixer/mill, and a weighed quantity of methanol (50 mL methanol weighed in a small-mouth flask on an electronic balance) was poured into the milling vessel. The lid was sealed to the vessel and the sample was milled for 30 min; the contents were heated to near the boiling point of methanol. The vessel was set aside for 1½ hr to allow the residue from seed to settle and to allow vessel and contents to equilibrate to room temperature. Centrifugation for 15 min at 1500-2000 rpm also could be used to reduce settling time. A glass syringe with a 5.1-cm 20 gauge needle was used to remove 2-10 mL aliquots of the methanol-extracted water mixture which were immediately injected through the rubber stoppers of the Vacutainer tubes. The stoppered end of each tube was then dipped into molten paraffin to immobilize the stopper and seal the hole made in the stopper by the syringe. Prior to use, the milling vessel, lid, balls, glass syringes and syringe needles were rinsed with methanol, heated in an air oven at 80 C for 1 hr, and cooled in a desiccator.

Titration

The Fisher K-F titrator was prepared for titration according to manufacturer's instructions. After reaching a stable endpoint with reaction vessel solution, a titer value (water equivalency) for the KF reagent was determined by injecting 0.1 g distilled water into the reaction vessel through the sample port using a 0.1-mL Hamilton syringe with a 10.2-cm needle. Before and after injection of water, the syringe was accurately weighed to the nearest 0.00001 g on the analytical balance. The water was titrated and the amount (mL) of Karl Fischer reagent used was noted. The water titer (F) in mg/mL was calculated as follows:

$$F = \frac{1000\,G}{A}$$

where G = grams of water used, and A = mL of Karl Fischer reagent used. This standardization procedure was conducted in triplicate and an average titer value determined.

An aliquot of sunflower seed methanol-extracted water mixture (containing ca. 10-75 mg water) was withdrawn from the Vacutainer tube into a 5- or 10-mL syringe with a 10.2-cm (20 gauge) stainless steel needle. The syringe with the methanol-water mixture was accurately weighed on the electronic balance (to the nearest 0.001 g); the mixture injected through the sample port into the reaction vessel, and the empty syringe reweighed. The water was titrated and mL of KF reagent used noted. The titration procedure was usually conducted in duplicate on each sample extract. The water content of the methanol used to extract the sunflower seed was determined in triplicate on 10-mL aliquots of methanol. Preliminary studies indicated that taking a 50-mL quantity of the methanol through the milling procedure was not necessary for methanol water determination since no detectable water was introduced during this process.

Calculations

The percent water (moisture content) is calculated using the equation:

$$\%\ \text{water} = \frac{(A_s - C) \times F \times 0.1}{M_e - (M_e \times R)} \times \frac{W_m}{W_s}$$

where A_s = mL of KF reagent required for titration of seed methanol-extracted water mixture, C = mL of KF reagent required for titration of water in methanol (blank), F = water titer, M_e = wt (g) of seed methanol-extracted water mixture titrated, W_m = wt (g) of methanol used for extraction of sample, W_s = wt (g) of seed extracted, and R = percentage residue in methanol-extracted water from extracted seed (W_s).

Blank titration value (C) for water in methanol used for extraction is determined by titrating weighed 10-mL volumes (triplicate) of methanol and is given by the equation:

$$\text{blank titer (C)} = \frac{A_m \times M_e}{M_m}$$

where A_m = mL KF required for titration of methanol blank (M_m), M_e = wt (g) of seed methanol-extracted water mixture titrated, and M_m = wt (g) of blank methanol (10 mL).

Experimental

Determination of residue. The residue, along with the water extracted from sunflower seed with methanol, is primarily oil and soluble carbohydrates, and the amount extracted will vary with the weight of the seed extracted (Fig. 1). To determine the residue in the methanol-extracted water mixture, 1-5 g of seed were extracted for 30 min with 50 mL of methanol with Spex Mixer/Mill. Then, ca. 10 mL of the mixture (weighed in a syringe) was transferred to a weighed aluminum moisture dish, and heated in a 60 C air oven until residue was dry (5-6 hr). The residue was cooled to room temperature and weighed. Four analyses were conducted for each sample size in duplicate. Percent residue (R) is calculated from the equation:

$$\% \text{ residue (R)} = \frac{\text{wt (g) dry residue} \times 100}{\text{wt (g) methanol-water mixture}}$$

Effect of sample size. KF moisture analyses were conducted on sunflower seed samples weighing from 1 to 5 g with moisture contents ranging from ca. 5.5 to 16.8%. The moisture content of each sample also was determined by the AOCS official method (7). Analyses were replicated 4 times in duplicate and data statistically analyzed.

Comparison of KF with oven methods. Six sunflower seed samples with moisture contents ranging from ca. 5.4 to 12.8% were analyzed for moisture content by automatic Karl Fischer titration; by AOCS official method Ai 2-75 using forced draft oven at 130 C for 3 hr (7); and vacuum oven method, 100 C for 20 hr at 30 mm Hg laboratory vacuum. KF and vacuum oven analyses were conducted on whole seed and on seed ground with equal weights of Hyflo Super Cel using Moulinex high-speed grinder (2½ min grinding).

Statistical analysis. Data were analyzed by analysis of variance and orthogonal polynomials for equally spaced treatments (i.e., sample size). Tests were performed with the statistical system described by Barr et al. (8). Significant differences between means were determined by Scheffé's multiple comparison procedure as described by Kleinbaum and Kupper (9).

RESULTS AND DISCUSSION

In extraction of sunflower seed with methanol by grinding in the Spex Mixer/Mill, two critical factors found were grinding time and seed-to-methanol ratio. Preliminary studies with seed-to-methanol ratio of 1:8 (on weight basis) indicated that a grinding time of 20-30 min was necessary to obtain satisfactory extraction. For all studies reported here, samples were extracted 30 min.

When sunflower seed is extracted with methanol in the Spex Mixer/Mill for 30 min, the temperature of the mill rises above the bp of methanol. Not only will the water in the seed be extracted but other components as well will be extracted from the high oil content seed including small quantities of oil and soluble carbohydrates. The mass of residue will have to be taken into consideration in the derivation of the moisture content calculation equation. The quantity of residue extracted was found to be linear and ranged from ca. 0.5% for 1 g seed to 1.1% for 5 g seed (Fig. 1).

The KF reagent is specific for water in the absence of interferences. In a study in which different quantities of water were added to methanol, a 100% recovery, within experimental error, of the water was obtained (Table I). However, when water was added to oven-dried seed (dried in forced draft oven for 4 hr at 130 C), recovery of actual added water was consistently 96-98.5% (average 97.2%) (Table II). This study was conducted on 3-g samples. Better recovery probably would be obtained on higher solvent-to-seed ratio but results are more variable for analysis of 1-g samples.

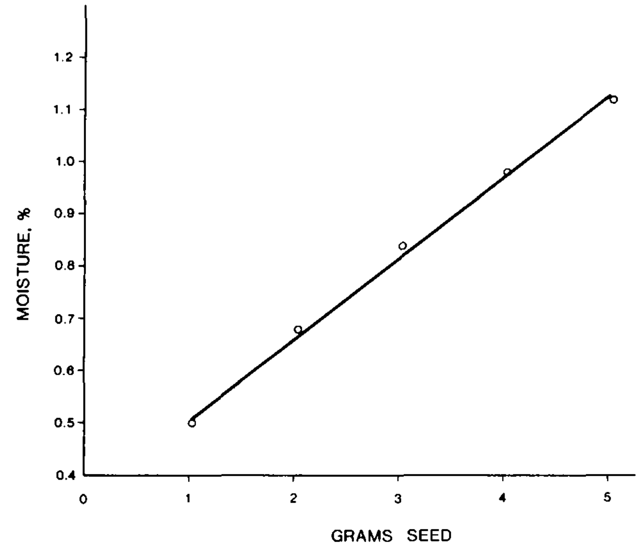

FIG. 1. Residue extracted into methanol-water mixture from sunflower seed.

The effect of sample size on Karl Fischer moisture analysis is shown in Figure 2. There were no significant differences ($P > 0.05$) in the analyses due to replication, therefore means were plotted. A highly significant difference in moisture content due to sample and sample size ($P < 0.0001$), respectively, were found. However, there was also a sample × sample size interaction ($P < 0.05$). This significant interaction was due to the linear decrease ($P < 0.05$) in moisture values obtained with KF at the 3-, 4- and 5-g sample sizes for sunflower seed moisture values of 12.88 and 16.70%, respectively, as analyzed by the AOCS method. This trend was also present in the sunflower seed samples with 10.54% moisture level. However, the values obtained

TABLE I

Karl Fischer Analysis of Water in Methanol[a]

Sample no.	Weight of water (g)	Weight of methanol (g)	Calculated water in methanol (%)	KF analysis, water in methanol (%)	Recovery (%)
1	0.505	8.109	5.86	5.83	99.5
2	0.642	8.071	7.37	7.39	100.3
3	0.826	8.105	9.25	9.27	100.2
4	1.010	8.097	11.09	11.07	99.8

[a] Analyzed in duplicate.

TABLE II

Karl Fischer Analysis of Water Added to Oven-Dried Sunflower Seed[a]

	Water content dried seed (%)	Water content of seed with added water (%)		
Sample no.	KF analysis[b]	Calculated %	KF analysis[b]	Recovery (%)
1	0.43	6.73	6.63	98.5
2	0.43	7.96	7.65	96.1
3	0.20	9.40	9.14	97.2
4	0.20	9.83	9.55	97.2
5	0.19	9.93	9.63	97.0
6	0.43	10.05	9.77	97.2

[a] Dried in oven at 130 C for 4 hr.

[b] Duplicate analysis of 3-g sample.

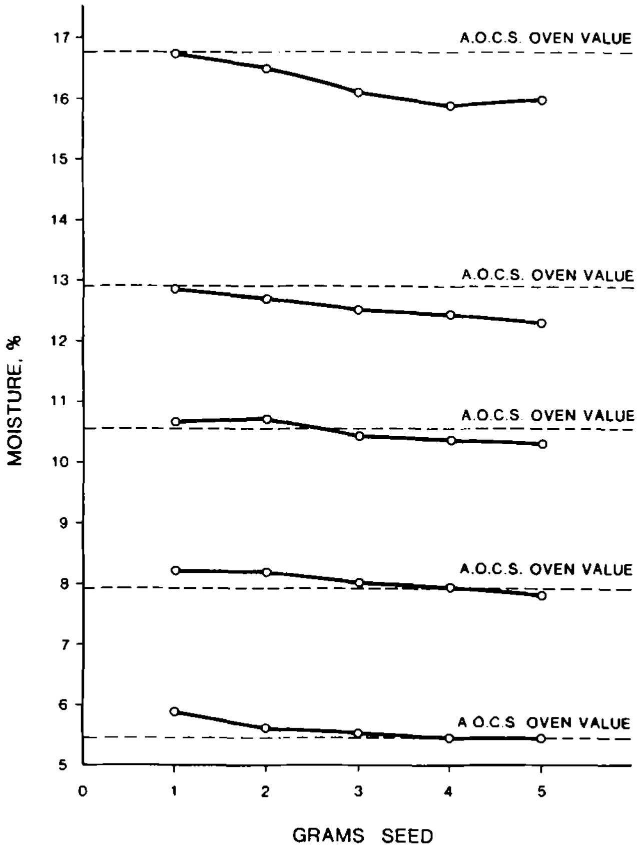

FIG. 2. Effect of sunflower seed sample size on Karl Fischer moisture analysis.

with KF for 3-, 4- and 5-g samples were not significantly different from the AOCS oven values.

In the moisture range of ca. 5.5-10.5%, the 3- and 4-g samples gave moisture values with KF that were closest to those obtained by the AOCS oven method. The average standard deviation for KF analyses was 0.31% for a 1-g sample and 0.14-0.20% for 2-5 g samples, whereas the standard deviation for AOCS moisture analyses was 0.11%. These data are in agreement with unreported data communicated by scientists from USDA, CMS, Grain Division who compared the measurements of the moisture in whole soybeans by six procedures. They found that, with beans of low moisture level (11.5%), KF and AOCS oven values were within ±0.3%. However, with beans of medium (12.5%) and high moisture (17.0%), KF values were lower by 0.5% and 1.0%, respectively.

Comparison of KF moisture analysis with oven analyses on whole and ground sunflower seed is shown in Table III. Analysis of variance indicated that there was no difference ($P > 0.05$) in moisture values due to method of analyses. However, there was a significant ($P < 0.02$) sample x sample type (i.e., whole vs ground seed) interaction for the analysis of moisture. This interaction is due to sample 1 (Table III) in which there was no difference in moisture values due to method of analysis or type of sample. However, for all other samples (i.e., samples 2-6), ground seed analyzed by KF and vacuum oven were significantly lower ($P < 0.05$) than that obtained on whole seed, regardless of the method used. The KF moisture values for whole sunflower seed generally were slightly lower than the AOCS forced draft and vacuum oven method values. The mean standard deviations for moisture determinations of the six whole sunflower seed samples were: 0.11% moisture content for KF analysis, 0.10% for vacuum oven method and

TABLE III

Comparison of Karl Fischer (KF) Moisture Analysis with Oven Methods on Whole and Ground Sunflower Seed

	Moisture (%)				
	Whole seed			Ground seed	
Sample no.	FD oven[a]	Vacuum oven[b]	KF	Vacuum oven[b]	KF
1	5.40[c]	5.43[c]	5.48[c]	5.13[c]	5.58[c]
2	7.12[c]	7.03[c]	7.09[c]	6.68[d]	6.76[d]
3	7.99[c]	8.01[c]	7.90[c]	7.23[d]	7.36[d]
4	9.78[c]	9.77[c]	9.57[c]	8.99[d]	8.83[d]
5	10.41[c]	10.31[c]	10.27[c]	9.94[d]	9.73[d]
6	12.67[c]	12.84[c]	12.63[c]	11.33[d]	11.48[d]

[a] Forced draft oven, AOCS Official Method Ai 2-75, 130 C for 3 hr (7).

[b] 100 C for 20 hr at 30 mm Hg.

[c,d] Means within rows with unlike superscripts differ ($P<0.05$).

0.05% for forced draft oven method.

In the oil analysis of sunflower seed by the AOCS Official Method Ai 3-75 and NIR method, the sample must be ground. Using KF and vacuum oven methods to measure moisture contents, sunflower seed were found to lose moisture (0.6% moisture from a sample containing 8.9% moisture) when grinding the sample with Hyflo Super Cel as in the AOCS official method (Table III). The loss was statistically significant and varies depending on the variety of seed and temperature and relative humidity of the laboratory during grinding. Therefore, moisture data obtained by instruments in which the seed have to be ground such as NIR may not be very accurate. Since sunflower seed are high in oil content (ca. 40-45%) and the oil has a high content of polyunsaturated fatty acids, moisture content of ground seed also cannot be accurately determined by air oven methods because of oil deterioration.

Although oven-drying methods are not specific for water (5), data presented in Table III show that oven moisture values accurately represent the true moisture of sunflower seed. Although the KF method is relatively rapid compared to the vacuum oven-drying method, it is not recommended for routine moisture analysis because of the time required for sample preparation (2 hr). However, as proposed by Jones and Brickenkamp (5) for moisture analysis of grains, the Karl Fischer method, as presented in this paper, should be the primary reference method for the determination of moisture in sunflower seed.

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✻Fatty Acids: Part 25.[1]

Chemical Transformations of C_{18} Furanoid Fatty Esters

M.S.F. LIE KEN JIE, S. SINHA and **F. AHMAD**, Department of Chemistry, University of
Hong Kong, Pokfulam Road, Hong Kong

ABSTRACT

Synthetic and natural C_{18} furanoid fatty esters were successfully converted to the corresponding furanoid alcohols, aldehydes, halides, ethers, acetates, mesylates, and chain extended by two carbon atoms in high yield to the corresponding C_{20} furanoid ester homologues. Acid hydrolysis of the furanoid esters furnished dioxostearate derivatives, which were cyclized with ammonium carbonate or ammonia in titanium chloride and with phosphorus pentasulfide to pyrrole and thiophene ester derivatives, respectively.

INTRODUCTION

In continuation of our studies of the properties of furanoid fatty acids and their derivatives, we now report the chemical transformations of the functional groups and the physical characteristics of such derivatives. Our ready source of a synthetic C_{18} furanoid ester (methyl 9,12-epoxyoctadeca-9,11-dienoate, **I**) is obtained from methyl ricinoleate, giving access to the 2,5-disubstituted furan system (2). The latex of the rubber plant *(Hevea brasiliensis)* furnishes the 2,3,5-trisubstituted furanoid ester (methyl 10,13-epoxy-11-methyloctadeca-10,12-dienoate,**II**) for this study (3). The objective of this exercise was centered on the ability to effect chemical transformation of the carbomethoxy group of the furanoid esters while retaining the furan system intact, and secondly to substitute the oxygen of the furan nucleus with other elements such as nitrogen and sulfur to yield pyrrole and thiophene derivatives, respectively.

DISCUSSION

The various chemical transformations involving the synthetic (2,5-disubstituted) and the natural (trisubstituted) C_{18} furanoid esters are outlined in Scheme I.

Reduction of the ester group to the corresponding alcohol (**III**) by $LiAlH_4$ was very selective and readily accomplished in high yield, without indication of any reduction of the furanoid nucleus. The furanoid alcohol (**III**) was converted to the chloroderivative (**IV**) using thionyl chloride and to the bromoderivative (**V**) using phosphorus tribromide. The iododerivative (**VI**) was prepared by the action of sodium iodide in acetone on the furanoid chloride (**IV**). Treatment of the furanoid alcohol (**III**) with acetic anhydride gave the acetate derivative (**VII**), and reaction of the furanoid bromide (**V**) with sodium ethoxide gave the ethyl ether derivative (**VIII**) in good yield. Chain extension by two carbons using the bromo derivative (**V**) with sodio malonate resulted in the production of a C_{20} furanoid ester homologue (**IX**) after decarbomethoxylation of the diester intermediate. The furanoid alcohol (**III**) was converted to the mesylate derivative (**X**) using methane sulfonyl chloride. Oxidation of the same furanoid alcohol (**III**) with chromic anhydride and pyridine complex resulted in the formation of the corresponding aldehyde derivative (**XI**). During all these transformations and reactions, the furan nucleus remained stable.

Similar reactions were conducted on the naturally occurring furanoid ester with similar success.

The acid-catalyzed ring-opening reaction of the furanoid

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[1] For Part 24, see reference 1.