

Figure 1. Relationship of refractive index to moisture in raisins, prunes, figs, and apricots

Results and Discussion

In the moisture range of 11 to 36%, refractive index was related to the moisture content of the dried fruits (Figure 1). (The graphs do not start at zero for the X and Y axes.) The refractive index correlated well—significant below the 0.001 level—with the vacuum oven moisture, as indicated by the correlation coefficient (Table I).

The refractive index readings can be translated to moisture content values by

solving a linear regression equation or by reading the values on a calibration curve based on the equation. Since a slightly hazy line is observed in the refractometer when the ground fruit is placed directly on the prism, a certain amount of subjectivity is inherent in the procedure. Therefore, each operator probably should prepare his own calibration line for each fruit.

The refractometric moisture method has the advantage of being simple and rapid. A nontechnical person can easily

make a determination in seconds, after the fruit is ground. In contrast, vacuum oven moisture determinations require a technically trained person, and the results cannot be obtained for 6 to 30 hours.

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MOISTURE BY GLC

Gas-Liquid Chromatography and Vacuum Oven Determination of Moisture in Fruits and Fruit Products

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The gas chromatographic estimation of water in fruits and dried fruit products is evaluated. A column of polyethylene glycol on polytetrafluoroethylene resolved water, 2-butanol (internal standard), and methanol. Peak area ratios are used to calculate moisture content. Results compare well with those of the vacuum oven method.

GAS CHROMATOGRAPHY has been reported to be a reliable method for determining the moisture of a number of materials. Workers at the National Bureau of Standards (7) have adapted gas-liquid chromatography to determine moisture in grains. Schwecke and Nelson (9) report its use in determining moisture of cereal products, raisins, and other materials. Kuwada (4) measured the water content of samples of hydrazine by GLC with satisfactory precision and accuracy. Harkin *et al.* (3) reported successful separation of water from azeotropes by chromatography on a

column of di(2-ethyl hexyl) phthalate on Celite 545 and his method affords quantitative measurements of the components. Bennett (7) pointed out that the usefulness of GLC for moisture analysis depends largely on preventing the water peak from tailing off. Columns of Teflon powders impregnated with various stationary phases reduce water tailing. The present investigation shows that water content of fruits and dehydrated fruit products can be determined by gas-liquid chromatography and compares results to those from the vacuum oven method.

Experimental

Materials Analyzed. Banana puree was prepared by blending peeled Chinese (Cavendish) bananas. Papayas were peeled, the seeds removed, and the remaining portion blended to a puree. Guavas were chopped in a Fitzmill, passed through a 0.033 pulper screen, then a 0.020 finisher screen to yield a smooth puree. Air-dried bananas were prepared from banana slices that had been dipped in SO_2 solution, then dried in a forced draft oven at 140° F. Drum-dried banana powder was prepared by drying banana puree on a double-drum dryer operated at 50 p.s.i. steam pressure

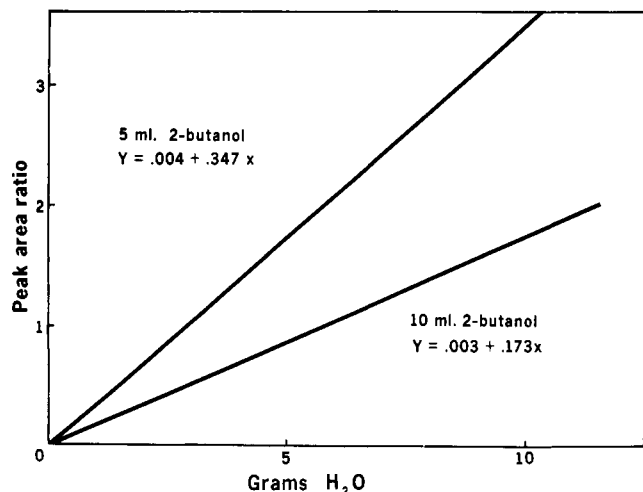


Figure 1. Moisture calibration for solvent systems with 5 ml. and 10 ml. of 2-butanol. The regressions of peak area ratio on grams of water

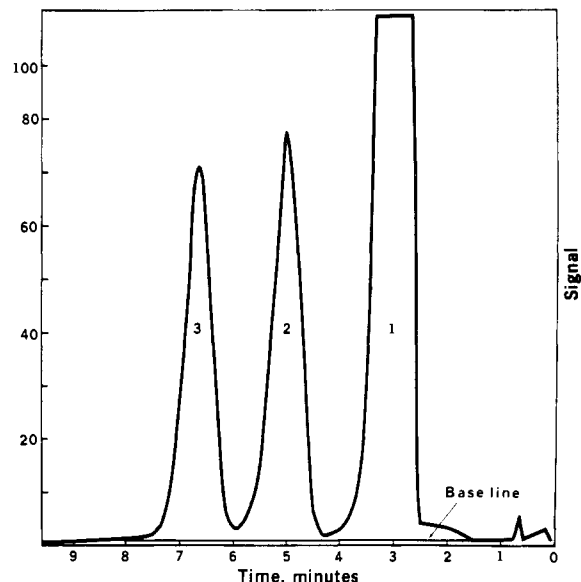


Figure 2. Chromatogram of material extracted from dried banana sample: (1) methanol, (2) 2-butanol, (3) water

and a residence time of about 20 seconds. Freeze-dried banana slices were prepared in a REPP Model 15 freeze dryer which employed a programmed temperature, 24-hour drying cycle. A synthetic fruit puree was made by blending 475 grams of water, 75 grams of sucrose, 2.5 grams of dried filter paper, 2.5 grams of pectin, and 1.0 gram of citric acid monohydrate. The mixture was blended to a homogeneous suspension that did not separate during several weeks' storage at 40° F. The moisture was calculated to be 83.7%, the pH 2.8, and the soluble solids 15.5% by refractometer.

Gas-Liquid Chromatographic Procedure. A portion of the sample to be analyzed was weighed into a glazed paper cup. The cup and sample were quickly transferred to a Waring Blendor jar (500 ml., screw-on lid) containing 100 ml. of anhydrous methanol and 5 or 10 ml. of anhydrous 2-butanol. For fresh fruit samples, 10 ml. of 2-butanol, and for dried materials, 5 ml. of 2-butanol proved satisfactory for the internal standard. The material was blended for 3 minutes, filtered rapidly through glass wool, and the filtrate held in a stoppered flask. A 10- μ l. syringe was used to deliver a 1- to 2.5- μ l. sample to the chromatograph; sample size depended upon the amount of water present. The weighing, blending, and filtration were completed easily in 10 minutes. Blank determinations gave values equivalent to 0.1 gram of water.

A thermal-conductivity instrument (Aerograph A-90 P) was used. The 10-foot column ($1/4$ -inch o.d. copper tubing) was packed with Fluropak 80 coated 10% by weight with Carbowax 400. Fluropak 80 was stirred in an acetone solution of the required amount of Carbowax 400, then dried in vacuo. The column was at 110° C., the injector at 150° C., and the detector at 200° C. Helium was passed through the column

at 65 ml. per minute and the chart speed was 25 mm. per minute.

Calibration curves were prepared by chromatographing samples containing various amounts of water in mixtures of 2-butanol (5 or 10 ml.) in 100 ml. of methanol. The known amount of 2-butanol in the solvent mixture provided the internal standard. Calibration curves, based on regression equations for two different volumes of butanol appear in Figure 1. The standard deviation of peak area ratios for the 5-ml. 2-butanol curve was 0.027, that for the 10-ml. curve was 0.013. Peak area was calculated as the product of peak height and the peak width at half the height. The base line for each chromatogram was drawn by connecting the flat portions of the curve immediately following the air peak with the flat portion after the water peak (see Figure 2). The area under the peak attributed to a compound is proportional to the weight % of the compound present in a mixture according to Dimbat, Porter, and Stross (2). The ratio of peak areas (water to 2-butanol) of an unknown sample is thus used to calculate the amount of water present in the sample. The chromatogram of the extract of a sample of dried banana is shown in Figure 2. The chromatograms of other fruit extracts were similar in nature.

Vacuum Oven Procedure. Stitt (7) discussed fundamental aspects of determining moisture content of foods and proposed that vacuum desiccation at room temperature be the primary reference method. However, this method may require weeks or months on materials high in sugar, so the vacuum oven method was selected as the reference in this study. Van Arsdel (17) pointed out that there are at least seven current vacuum oven procedures for moisture determination on food products. Makower and Neilson (5, 6)

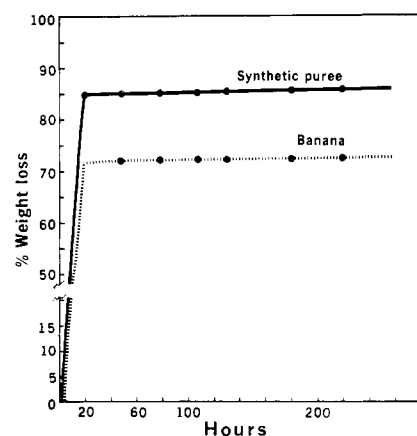


Figure 3. Curves for vacuum oven drying of fresh banana puree and synthetic fruit puree, 60° C., 1 mm. of Hg pressure

reported satisfactory results at 60° and 70° C. and recommended 60° C. for certain commodities susceptible to thermal degradation at higher temperatures. Nury, Taylor, and Brekke (8) measured the moisture content of dried fruits by means of a predrying followed by vacuum oven drying at 60° C. for 30 hours. The method of the present study was devised to avoid foaming and spattering of fresh fruit samples and to minimize thermal degradation.

Samples were weighed into aluminum moisture dishes containing sand and a small stirring rod. The sample was stirred into the sand, 5 ml. of 95% ethanol were added, and the sample was brought to near dryness on the steam bath before vacuum drying began. Drum-dried and freeze-dried material was not predried in this fashion.

Vacuum drying was carried out at 60° C. and 1 mm. of Hg pressure for 30

Table I. Moisture Contents of Fruits and Fruit Products as Determined by Vacuum Oven and Gas-Liquid Chromatography

Vac. oven	Moisture Content, (%)				s^a
	\bar{X}	s^a	GLC	\bar{X}	
GUAVA					
87.22			86.76		
87.39			86.21		
87.30			86.53		
87.27	(87.30)	0.08	88.55	(87.01)	1.05
PAPAYA					
87.17			85.50		
87.17			84.54		
87.21			88.29		
87.20	(87.19)	0.02	88.08	(86.60)	1.87
FRESH BANANA					
69.70			72.69		
69.69			68.05		
69.70			69.42		
69.54	(69.66)	0.08	71.15	(70.33)	2.04
AIR-DRIED BANANA					
18.13			18.63		
18.27			18.41		
18.37			19.07		
18.69	(18.37)	0.23	19.60	(18.93)	0.52
DRUM-DRIED BANANA					
4.24			4.18		
4.19			3.73		
4.27			4.24		
4.20	(4.23)	0.02	4.38	(4.13)	0.28
FREEZE-DRIED BANANA					
4.22			4.53		
4.26			4.62		
4.37			4.34		
4.30	(4.29)	0.06	4.54	(4.51)	0.12
RAISIN					
15.33			17.16		
14.92			16.43		
15.71			17.05		
15.89	(15.46)	0.43	17.10	(16.94)	0.34
SYNTHETIC PUREE					
82.93			83.23		
83.04			82.13		
83.00			82.48		
83.00	(82.99)	0.08	82.50	(82.59)	0.57

^a Standard deviations of quadruplicate assays.

hours. In early experiments, duplicate samples of banana puree and the synthetic fruit puree were withdrawn at the intervals indicated on Figure 3. After 30 hours of drying, the moisture assay was within 0.5% of that after 260 hours of drying.

Results

Each material was analyzed in quadruplicate by each of the two methods (Table I). The reproducibility of the vacuum oven method is generally better. The GLC method gave more reproducible results on the dehydrated products than on the fresh fruits. The greatest discrepancy between methods was 5% in the results on freeze-dried banana slices where the vacuum oven method gave the lower value. Whole

slices of freeze-dried banana were analyzed because comminution of slices invariably involved absorption of moisture from the air. With such large pieces, not all of the moisture may have reached the surface. This points up an additional advantage of the GLC method—whole pieces were easily extracted with solvents. Neither method gave consistently higher results than the other. From the materials used to make the synthetic puree, one calculates the moisture content to be 83.7%. The vacuum oven assay gave 82.99% and the GLC method 82.58%, leading one to conclude that, for this sample, the vacuum oven was more accurate.

Chromatograms of the solvent system containing the following substances showed that they would not interfere in

the assay method: ethanol, acetic acid, ethyl acetate, methyl butyrate, 2-pentanone, amyl alcohol, amyl acetate, ethyl hexanoate, and malic acid.

Simple precautions such as rapid weighing, blending in a covered container, rapid filtration, and drying apparatus between uses keep water absorption from becoming a problem. Blendor cups were rinsed with methanol and acetone and allowed to dry before using.

Columns consisting of 10% Carbowax 1540 on Fluropak 80, and 10% Carbowax 400 on Chromosorb G, gave unsatisfactory results because the water peak tailed off. As can be seen in Figure 2, a column of 10% Carbowax 400 on Fluoropak 80 gives sharp, symmetrical peaks with negligible tailing of the water peak.

The GLC method for moisture determination as described here provides a rapid, simple means of measuring the moisture that can be extracted from fruits by methanol. For the kinds of materials analyzed the method gives results within 3% of those given by the vacuum oven.

Acknowledgment

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