the second standard solution onto the samples and make to volume with 1% hydrochloric acid solution. Shake intermittently over a 30-minute period. Allow the heavy particles to settle and filter the extract with suction through a 1/4-inch mat of Super-Cel held on a filter paper in a Büchner funnel. Use a 60-mm. internal diameter, Büchner funnel and a 250-ml. suction flask, and filter paper (S & S 597, 5.5 cm.). Discard the first few milliliters of filtrate used to wet the mat of Super-Cel. The filtrate must be clear. Treat as described under "Standard Curves" starting with "transfer a 5.0-ml. aliquot."

Analysis of Samples. Samples are handled as described for standard curves, without the addition of the cadmium anthranilate. A blank should be run with each set of samples, just as the blank with the standard curve was run. A large amount of the blank feed should be kept on hand and used as such for all medicated feed analysis. The blank feed serves to duplicate the conditions that are present in the feed containing the medicament.

Discussion. Analysis of feeds containing cadmium anthranilate should pose no problem as to interfering materials, because no other medicament has been approved for use in the same feed. The method described removes interferences that are normally present in feeds. The blank made from the laboratory prepared blank feed further reduces chances for error. The standard curve itself, being prepared in the presence of a blank feed, serves as proof of recovery of the material from feeds. Additional recovery data are presented in Table I. All data were collected using a Beckman DK-2 ratio recording spectrophotometer.

Table I. Recovery of Cadmium Anthranilate from Blank Feed

Cadmium Anthranilate in Final Aliquot		Recovered,
Added	Recovered[a]	%
10.0	10.0	100.0
20.0	20.0	100.0
30.0	29.0	96.6
40.0	39.0	97.5
50.0	47.5	95.0

[a] Average of 4 determinations.

An $E^{1\%}_{1\ cm.}$ value of 1737 from a theoretical standard curve compares well with an $E^{1\%}_{1\ cm.}$ value of 1710 as calculated from a standard curve made in the presence of a feed extract. An $E^{1\%}_{1\ cm.}$ value of 2427 is reported for arsanilic acid by Senn and Woolford (*6*). Merwin (*3*) reports that feeds containing large amounts of tryptophan tend to give high blanks when the method is used for determining arsanilic acid. The same possibility exists here, but to a large extent is obviated by the use of a feed blank as previously discussed.

Acknowledgment

The cadmium anthranilate used in this study was supplied by Dr. Hess and Clark, Inc., Ashland, Ohio.

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Received for review July 30, 1958. Accepted January 30, 1959. Division of Agricultural and Food Chemistry, 135th Meeting, ACS, Boston, Mass., April 1959. Project No. 1039, Texas Agricultural Experiment Station.

DRIED FRUITS STABILITY

Modified Direct Colorimetric Method for Determination of Sulfur Dioxide in Dried Fruits

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A simple and direct colorimetric method for the determination of sulfur dioxide in dried fruits can be conveniently used in the field, as well as in the laboratory. The procedure is rapid and reproducible, giving values comparable with those obtained by the gravimetric Monier-Williams technique.

PRECISE DETERMINATION of sulfur dioxide in dried cut fruits and golden, bleached raisins is important to the dried fruit industry. To enhance the stability of these products, it is necessary to maintain the sulfur dioxide content above certain minimum levels. Analytical procedures commonly used now are the gravimetric method of Monier-Williams (*1*) and the iodometric method of Nichols and Reed (*8*). These methods include a distillation operation, and the Monier-Williams method is rather involved and time-consuming for some industrial applications. A simpler procedure for sulfur dioxide analysis has been sought for some time.

Detailed reviews of the chemistry and analytical methods for sulfur dioxide in foods have been published by Joslyn and Braverman (*7*) and Gehman and Osman (*4*). A number of iodometric methods have been described (*2, 9, 10*) for sulfur dioxide determination in dried fruits and vegetables. Colorimetric methods for the determination of sulfur dioxide in some food products have also been reported by several authors (*3, 5, 6, 11*). These methods are based on Steigman's (*12*) technique for the determination of sulfuric acid by modification of the well-known reaction for the detection of aldehydes with the colorless solution of fuchsine–sulfurous acid.

Very recently West and Gaeke (*14*)

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described a method for the colorimetric determination of atmospheric sulfur dioxide by its fixation in sodium tetrachloromercurate to form a stable, complex, disulfitomercurate ion $[Hg(SO_3)^2]^{--}$, which was subsequently treated with the dye pararosaniline hydrochloride and formaldehyde to give a colored solution. In 1957, Stone and Laschiver (*13*) reported on a sensitive colorimetric method for the determination of traces of sulfur dioxide in beer, using pararosaniline hydrochloride and formaldehyde for their color development.

The method here presented is a modification of that of West and Gaeke (*14*) as elaborated by Stone and Laschiver (*13*). It may prove useful in field work for growers and packers of dried fruits, because the samples can be prepared in the field and held in the stabilizing solution (sodium tetrachloromercurate) for several days prior to analysis (Figure 1).

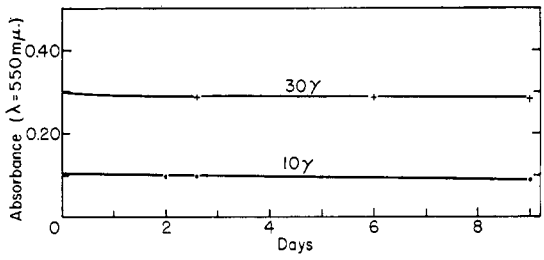

Figure 1. Stability of sulfur dioxide solutions in sodium tetrachloromercurate reagent

Table I. Determination of Sulfur Dioxide in Dried Fruits

Fruit	Method: Colorimetric,[a] 10-G. Sample, P.P.M.		Monier-Williams Gravimetric, 25-G. Sample, P.P.M.		Nichols and Reed Iodometric, 32-G. Sample, P.P.M.	
Apricot	3090	3100	3120	3190		
Apple	1030	1015	1020	1090		
Peach	2145	2165	2160	2180		
Peach	2810	2800	2870		2930	2930
Pear	1090	1105	1090	1110	1190	1330
Apricot	2460	2475	2420	2480	3145	2590
Peach	1270	1285	1340	1460	1610	1350
Apricot	1675		1730	1750		
Golden raisin	1215	1240	1320	1400	1380	
	Replicate Colorimetric Analyses					
Apricot	3140		3230		3230	
Apple	980		965		1000	
Peach	1545		1560		1595	
Pear	1070		850		1050	
Apricot	1280		1230		1330	
Golden raisin	820		805		805	
Apricot	2450		2450		2570	

[a] Replicates taken after blending.
[b] Precision is approximately ±1% of reported value.

Materials and Methods

Reagents. Formaldehyde solution, 0.015%, prepared from 40% formaldehyde.

Acid-bleached pararosaniline hydrochloride. Place 100 mg. of pararosaniline hydrochloride (National Aniline Division, Allied Chemical and Dye Corp.) and 200 ml. of distilled water in a 1-liter volumetric flask. Add 160 ml. of hydrochloric acid (1 to 1) and bring to volume with distilled water. Let stand overnight before use.

Sodium tetrachloromercurate, stabilizing solution, prepared by the method of West and Gaeke (*14*). Place 23.4 grams of sodium chloride, reagent grade, and 54.3 grams of mercuric chloride in a 2-liter volumetric flask. Add about 1900 ml. of distilled water and shake to dissolve. Bring to volume with distilled water.

Preparation of Sample. Place 10 grams of dried fruit (ground or whole) in a blender containing 290 ml. of water. Blend for 3 to 5 minutes. Withdraw a 10-gram aliquot from the bottom of the blender with a 10-ml. calibrated free-running pipet, and transfer to a 100-ml. volumetric flask containing 4 ml. of the 0.5*N* sodium hydroxide solution. Swirl and mix (about 15 to 30 seconds) to dissociate bound sulfur dioxide. Add 4 ml. of the 0.5*N* sulfuric acid solution, followed by 20 ml. of sodium tetrachloromercurate (stabilize the sulfur dioxide in the complex ion form). Bring to volume with water. In the case of dried apples, 2 ml., and in the case of golden bleached raisins, 1 ml. each of base and acid, are required. All other steps are the same as above. At this point the analysis may be delayed if desired. Filter through Whatman No. 2 or equivalent paper, or allow to settle for decantation.

Colorimetric Analysis. Place a 2-ml. aliquot of the filtrate or supernatant liquid in a test tube (25 × 200 mm.) containing 5 ml. of pararosaniline hydrochloride. Add 10 ml. of the aldehyde solution, mix, and allow to stand at room temperature for 20 to 30 minutes. Determine the absorbance in a calibrated colorimeter tube (12 × 100 mm.) at 550 to 570 mμ, with a blank set at 100% transmittance, and calculate the micrograms of sulfur dioxide from the standard curve.

Carry out blank determination on the fruit in the same way, but use 10 ml. of water in place of the aldehyde solution.

Calculate parts per million of sulfur dioxide in the sample as follows:

$$\text{P.p.m. } SO_2 = \gamma\ SO_2 \text{ (from standard curve)} \times 150$$

This procedure can be used to estimate the free sulfur dioxide content of dried fruits, if, in the preparation of the sample the base and acid are omitted, and the analysis is carried out without delay.

Standard Curve Calibration. Prepare a solution containing 100 γ of sulfur dioxide per ml. from pure sodium bisulfite (58.5% assay as sulfur dioxide) Standardize with 0.01*N* iodine solution before use.

Into a series of 100-ml. volumetric flasks, containing 20 ml. of sodium tetrachloromercurate, pipet different volumes of the bisulfite solution, so that when brought up to volume each flask will contain varying amounts of sulfur dioxide, ranging from 0 to 50 γ per ml. Use 2 ml. of these solutions for colorimetric analyses as described above. A plot of micrograms of sulfur dioxide *vs.* absorbance shows that the system follows Beer's law in the range 0 to 40 γ.

Results and Discussion

The method is accurate over the range of 0 to 40 γ of sulfur dioxide per ml. With concentrations to about 15 p.p.m., maximum color development is reached after 20 minutes at room temperature; above 15 p.p.m., a 30-minute period is required. Once developed, the color is stable for about 15 minutes.

The method is uniform for all dried fruits, except that in the case of golden bleached raisins and dried apples the volume of the base and the acid used in the analysis is less than that required for other dried fruits.

No sulfur dioxide losses were observed during the recommended blending time. This was determined by gravimetric Monier-Williams analyses of several blended and unblended dried fruits. The error introduced by the transfer of a 10-gram aliquot with a calibrated pipet from the blender was found to be small, with a coefficient of variation of 1% in 10 trials of different dried fruits.

It was found that blank samples from a filtrate gave fairly constant values of about 0.02 in absorbance against water. Somewhat higher and inconstant values were obtained when the supernatant liquid was used. It is, therefore, possible for the estimation of sulfur dioxide content of dried fruits to use water for the 100% transmittance setting, whereupon a correction is applied to the absorbance readings.

The colorimetric method was compared with the methods of Nichols and Reed (*8*) and Monier-Williams (*1*). The results (Table I) indicate good agreement between the colorimetric and gravimetric Monier-Williams methods. The Nichols and Reed values were in every case higher than the values obtained by the other procedures. This may be due to the fact that no correction was made for blank samples, as unsulfured dried fruits were not available. It has been reported (*9*) that blank determinations by the Nichols and Reed procedure, may run to about 200 p.p.m. in some dried fruits.

Table I also presents replicate sulfur dioxide values on analyses of various dried fruits. The results indicate the adequate reproducibility of the colorimetric procedure.

Acknowledgment

The authors are indebted to D. W. Sanshuck for assistance with the gravimetric analyses.

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Received for review August 11, 1958. Accepted December 24, 1958. Mention of specific products does not constitute endorsement by the Department of Agriculture.

SUGAR IMPURITIES

Composition of "Floc" Formed in Acidified Sirups from Refined Granulated Cane Sugars

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Refined granulated cane sugar occasionally contains trace amounts of material which gradually precipitates from acidified sirups. This "floc" is undesirable in bottled beverages. Its major components are starch, lipides (wax), protein, ash constituents, and decolorizing carbon from the refining operation. Carbon and the organic components predominate. Silica is the major ash constituent. Possible test procedures for estimating floc in refined cane sugars were investigated. An improved procedure adapted from a floc test currently used in the beverage industry appears to offer the most promise.

ALTHOUGH REFINED SUGAR from both sugar cane and sugar beets is one of the purest industrial chemicals available, it occasionally contains a few parts per million of material which gradually precipitates from acidified sugar sirups. The precipitate, "floc," is undesirable in bottlers' concentrates, bottled drinks, and acidic pharmaceutical sirups.

Some progress has been made in alleviating the floc problem of refined beet sugar by modification and improvement of the processing methods, based on the findings (*9, 26*) that a saponin and its derivatives are chiefly responsible for this type of floc. The present investigation was undertaken to obtain information on the nature and composition of cane sugar floc and to explore possible methods for its estimation.

Sugars Used in Investigation

Commercial samples, including both flocculating and nonflocculating cane sugars, were obtained through the cooperation of members of the bottling and sugar refining industries. The five refined granulated sugars used for the isolation of floc were selected because they produced moderate to heavy floc in low pH sirups and were representative of different commercial refining processes. The processing histories and some compositional characteristics of the five sugars are given in Table I. The data reported are for the same components found in cane sugar floc.

Ash was determined by charring and incinerating the sugar in the presence of sulfuric acid at 550° C., following essentially the procedure of Valdez and Camps-Campins (*24*). Starch was determined colorimetrically as the starch-iodine complex in dilute perchloric acid solution by a slightly modified Balch procedure (*2-4*), adapted from Pucher *et al.* (*13, 19, 20*). Sweet potato starch of known purity was used as a standard. Soxhlet-extraction of 200 grams with chloroform for 42 hours, followed by processing the extract according to Browne and Zerban (*5*), was employed for determining wax. Protein content was calculated from total nitrogen values obtained by Kjeldahl digestion and by colorimetric evaluation using a special Nessler reagent (*25*). The relative amounts of decolorizing carbon (free carbon) were estimated by dissolving 25 grams of sugar in 100