

content and decrease in percentage germination (4) on storage, the moisture content of cottonseed reserved for seeding purposes should be considered also and be low enough to insure good preservation.

Summary

The relationship of the free fatty acid content in the oil to the percentage germination for 254 samples of cottonseed of different varieties indicates that the free fatty acid content may be used as a practical screening index for use in selecting lots of cottonseed to be reserved for seeding purposes and subsequent testing for germination. The percentage germination decreases in general with increasing free fatty acid content. The mathematical probability that a given lot of seed will exceed a specified minimum germination value decreases markedly as the free fatty acid

content of the oil increases. Insofar as practical, it is suggested that cottonseed reserved for seeding have a low free fatty acid content, less than 0.75% in the oil if at all possible.

Acknowledgments

The authors wish to acknowledge with thanks the assistance of Claire Lesslie and Lloyd G. Burkenstock Jr. in determining the free fatty acid values.

REFERENCES

1. American Oil Chemists' Society, Official and Tentative Methods, 2nd Ed., edited by V. C. Mehlenbacher, Chicago, 1946.
2. Hoffpauir, C. L., Petty, D. H., and Guthrie, J. D., *Science*, **106**, 344 (1947).
3. Meloy, G. S., *Oil and Soap*, **16**, 174 (1939).
4. Simpson, D. M., *J. Agr. Res.*, **64**, 407 (1942).

[Received July 25, 1950]

A Colorimetric Method for Water-Soluble Silicates in Detergents¹

WILLIAM J. MILLER, The Procter and Gamble Company, Ivorydale, Ohio

THIS method grew out of the need for a rapid, fairly accurate control method to make occasional determinations for silica on the crutcher mix and the finished soap products. The method worked so well that it was expanded to cover the analysis of all types of detergents, even those highly built with phosphates. If the assumption may be made that water-soluble silica is the same as the total silica, the method is just as accurate as the dehydration method. When an appreciable amount of water-insoluble silicate is present, the method may be modified to include a determination of this material. When only a roughly accurate control is required, the amount of silica that is water-insoluble may generally be ignored.

Discussion

The method is based on the development of the yellow silico-molybdic acid complex. Although some workers (4) have suggested that the reduction to the blue complex affords better detection of smaller quantities of SiO_2 (in the range of a few p.p.m.), it was felt that the range of concentrations to be encountered as applied to detergents did not warrant the use of this modification. Moreover the interference of phosphorus is greater and more difficult to eliminate when the blue color is developed.

Citric acid was found to be an excellent bleach for the yellow phospho-molybdic acid color, having no effect on the color produced by silica. Knudson (3) first precipitates the phosphates with calcium chloride but shows that the pH at this point is quite critical and requires a buffer to keep the pH of the solution at 10.0 before precipitation.

Figure 1 is a curve showing the development of the color from silica alone while Figure 2 shows the additional effect of phosphorus followed by the addition of citric acid. It was found that the amount of citric acid prescribed by the method would completely eliminate the effect of 25 times as much P_2O_5 as SiO_2 . Table I indicates that the proposed method is as good

as the dehydration method and a series of duplicate analyses show the standard deviation to be $\pm 0.05\%$ for samples containing 1.5 — 5% SiO_2 and $\pm 0.01\%$ for samples containing up to 1.5%.

Apparatus

1. Klett-Summerson colorimeter.
2. No. 42 Klett-Summerson filter.
3. 2 x 4 cm. absorption cells.
4. Burettes, pipettes, volumetric flasks, etc.

Reagents

1. Neutral, 95% 3A or No. 30 alcohol.
2. Ammonium molybdate solution. 10% $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot \text{H}_2\text{O}$ in water.
3. Citric acid solution. 10% $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ in water. Small quantities should be prepared so that the solution being used is not more than a week old. What little mold forms within this time should be filtered off before the reagent is used.
4. Sulfuric acid. 1:4 in water.
5. Standard silica solution (1 ml. = 0.0002 gm. SiO_2). Fuse 0.2000 gm. of pure SiO_2 in 2 gms. of Na_2CO_3 — K_2CO_3 fusion mixture for about 15 minutes. Cool and dissolve in warm water, using a platinum dish for a container. Cool the solution and transfer to a 1,000-ml. volumetric flask. Make to volume without delay and store in a wax lined or hard rubber bottle.

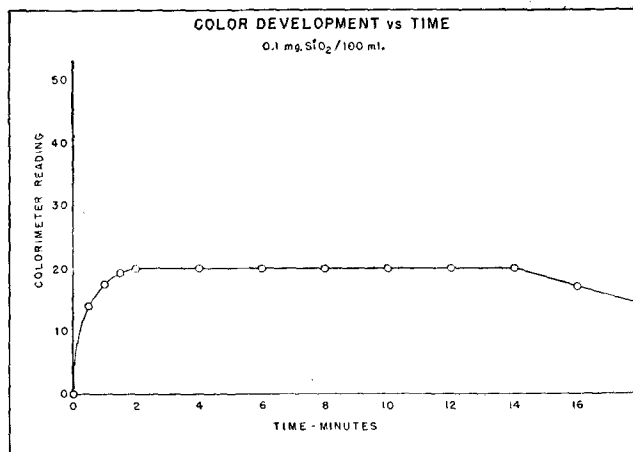


FIG. 1.

¹ Presented at the fall meeting, American Oil Chemists' Society, Oct. 31-Nov. 2, 1949, Chicago, Ill.

Preparation of Calibration Curve

Add, from a microburette, to 100-ml. volumetric flasks, amounts of the standard silicate solution to cover a range from zero to 1.0 milligram of SiO_2 . Add enough water to each flask to make the total volume about 50 ml. and, from pipettes or burettes, add 1.0 ml. of 1:4 H_2SO_4 and 5.0 ml. of 10% molybdate solution.

Allow the color to develop for 2 to 3 minutes and add 5 ml. of 10% citric acid solution (note 1); make to volume with water and measure through a 20-mm.

TABLE I
Typical Analyses

Sample	Total SiO_2 by Dehydration	Water-Insoluble Material	Water-Soluble SiO_2 by Dehydration	Water-Soluble SiO_2 by Proposed Method
Synthetic "A".....	5.02%	1.42	3.65	3.65
Synthetic "B".....	4.95	2.45	2.53	2.55
Bar Soap "A".....	0.152	0.150	0.151
Bar Soap "B".....	0.160	0.158	0.159
Bar Soap "C".....	0.148	0.150	0.148
Bar Soap "D".....	0.157	0.158	0.158
Flake Soap "A".....	1.44	1.43	1.45
Flake Soap "B".....	1.44	1.44	1.44
Soap Powder "A".....	4.22	4.22	4.22
Soap Powder "B".....	3.02	3.01	3.01

absorption cell in a Klett-Summerson colorimeter at 420 $\text{m}\mu$. The instrument should be balanced against a similar solution of reagents containing no silica at zero. A large number of standards should not be handled at one time since the absorption must be measured within 10 minutes after addition of the citric acid. Plot colorimeter reading against milligrams of SiO_2 and calculate the slope of the curve for making measurements of unknowns, or use the curve directly (see Calculations).

Preparation of the Sample

Built Synthetics. Transfer $5 \pm .001$ gm. of sample into a 400-ml. beaker and add about 200 ml. of freshly boiled, hot, neutral 95% alcohol. Cover with a watch-glass and heat on a steam bath for 10 minutes with occasional vigorous stirring. Filter through a Gooch crucible² and wash with 200 ml. of the hot alcohol. Discard the alcoholic filtrate and rinse out the suction flask with water. Replace as before and to the residue in crucible rapidly add boiling water. Wash the water-insoluble material with boiling water until 75 to 100 ml. have been added. Transfer the filtrate to a 500-ml. volumetric flask, cool to room temperature, and make to volume. Transfer a 50-ml. aliquot to a second 500-ml. volumetric flask, make to volume, and use 10-ml. aliquot for the colorimetric determination. Other dilutions are permissible, but the final aliquot should be between 5 and 50 ml. and represent between 0.1 and 1.0 mg. SiO_2 . Ignite the crucible² and contents if total SiO_2 is desired.

Bar Soap, Flakes, and Powders. The same procedure is followed as for synthetics except that the sample should be dissolved in alcohol on a steam bath. It is well to slice bar samples into thin pieces. Filter, while hot, through Whatman No. 41 paper and wash with hot alcohol. The alcohol insoluble

² Total silica may be assumed to be the sum of the ignited water-insoluble portion and the water-soluble SiO_2 . If this figure is desired, the Gooch crucible must of course be ignited and weighed before filtration. The precipitate may be ignited directly, if speed is important, without preliminary oven drying.

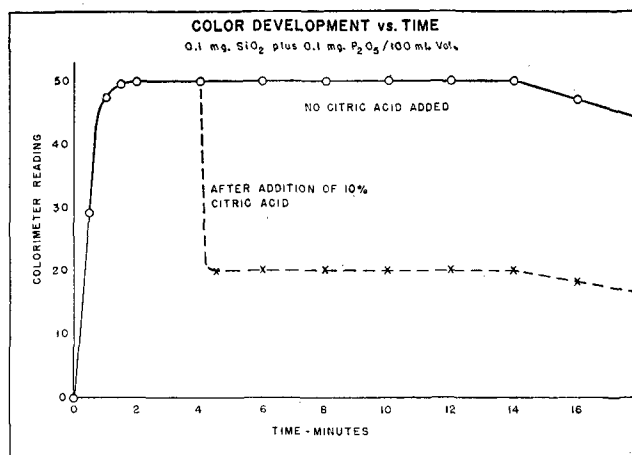


FIG. 2.

residue is washed through the paper with hot water into a 250-ml. volumetric flask. Five- to 50-ml. aliquots representing 0.1 to 1.0 mg. SiO_2 should be used for the colorimetric test. The water-insoluble residue in the paper may be determined by ashing if a total SiO_2 figure is desired.

Determination

Transfer a suitable sized aliquot (see Preparation of the Sample) to a 100-ml. volumetric flask. Add enough water to make the total volume, about 50 ml. From pipettes or burettes, add 1.0 ml. of 1:4 H_2SO_4 and 5 ml. 10% ammonium molybdate solution, in that order. Mix and allow the color to develop for 2 minutes. Add 5 ml. of 10% citric acid (note 1) from a pipette and make to volume with water. Mix well and measure the absorption in a Klett-Summerson colorimeter in a 20-mm. cell at a wave length of 420 $\text{m}\mu$. Not more than 5 minutes should elapse between the time the citric acid is added and the absorption measured. The instrument should be balanced against a blank at zero on a solution containing only water, H_2SO_4 , molybdate, and citric acid as in the preparation of the calibration curve.

Calculations

Figure 3 shows the type of calibration curve that should be obtained and will be used to illustrate the following examples:

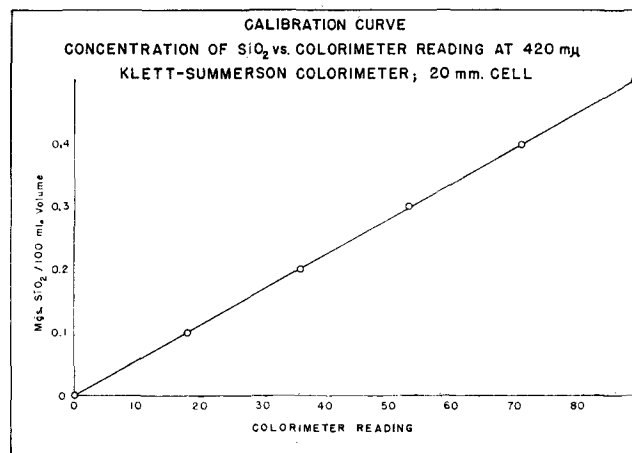


FIG. 3.

1. Mg. of SiO_2 from calibration curve $\times 0.1 \div$ gm. of sample in final aliquot = % SiO_2 .

Example:

Aliquot contains 0.01 gm. sample

Colorimeter reading = 76

Mgs. SiO_2 from calibration curve = 0.435

$(0.435 \times 0.1) \div 0.01 = 4.35\% \text{SiO}_2$.

2. Slope of curve \times colorimeter reading $\times 0.1 \div$ gm. of sample in final aliquot = % SiO_2 .

Example:

Slope of curve = 57.25×10^{-4}

Aliquot contains 0.01 gm. of sample

Colorimeter reading = 76

$0.005725 \times 76 \times 0.1 \div 0.01 = 4.35\% \text{SiO}_2$.

Notes

1. This method may of course be applied to samples containing no phosphate. In such a case the citric acid bleach may be eliminated from the procedure. If this is done, the calibration curve should be prepared without the citric acid. However, if a laboratory plans to use the method for various products, some of which may be built with phosphates, it is simpler to prepare a single calibration curve using citric acid and then use the citric acid procedure for all samples.

2. The recommended use of this method is with a photoelectric colorimeter. However as a semi-quantitative test to check the limits on a product, the silico-molybdate color may be compared visually with two ampules of picric acid solution representing the upper and lower limits of silica allowed. Twenty-five and six tenths mg. of vacuum dried picric acid per liter is equivalent to 50 mg. of SiO_2 per liter. Standard silica solution may be used as a standard, but the color has no permanence. Picric acid solutions, if protected from evaporation, may be used indefinitely.

3. Advantage may be taken of the double color development, before the addition of citric acid, quantitatively to determine orthophosphate. Measurement of the color should be made, before the addition of citric acid, at 420 m μ . After the final measurement is made of the bleached color, the difference between the two colorimeter readings may be taken as the color due to orthophosphate. A calibration curve should be prepared using standard NaH_2PO_4 solution and the standard silicate solution.

It must be remembered that the phosphorus color will be due to orthophosphate only and that the color will not be stable when polyphosphates are present. The color development takes place in acid medium which favors hydrolysis.

Summary

Water-soluble silica is determined rapidly and accurately by measuring the color produced after the development of silico-molybdic acid. Citric acid is used to eliminate any interference from phosphate builders. The entire procedure requires not more than 30 minutes and is applicable to both soaps and synthetic detergents. Semi-quantitative estimation between limits may be carried out even more rapidly by using picric acid standards and a visual comparator.

Acknowledgment

The author expresses grateful acknowledgment to Procter Thomson who initiated this work by pointing out the need for such a method.

REFERENCES

1. W. H. Hadley, *Analyst*, **66**, 486 (1941).
2. W. H. Hadley, *Ibid.*, **67**, 5 (1942).
3. H. W. Knudson, *et al.*, *Ind. Eng. Chem., Anal. Ed.*, **12**, 270 (1940).
4. M. C. Schwartz, *Ibid.*, **6**, 364 (1934).

[Received November 7, 1949]

Report of the Uniform Methods Committee

1. At the 23d Fall Meeting in Chicago, November 1, 1949, the Seed and Meal Analysis Committee recommended for adoption as tentative, a new Method Ad 1-48, for sampling tung fruit, and new Methods Ad 2-48, Ad 3-48, Ad 4-48, and Ad 5-48, for analysis of tung fruit and kernels. These methods were adopted as tentative.

2. The Soap Analysis Committee decided to change the esterification flask in Method Da 12-48 (A-1) from 150 ml. to 125 ml. capacity as the latter size is more readily obtainable. Approval of this change was voted by the Society.

3. The Refining Committee, in response to a request from the Department of Commerce, Bureau of the Census, submitted the following as a proposed definition for a refined vegetable oil:

A refined vegetable oil or fat is one which has been processed so as to reduce the coloring matter and remove substantially all of the free fatty acids, phosphatides, gums, and insoluble impurities.

This definition represented a composite or consensus of definitions submitted by individual members of the Refining Committee and agreed upon by a subcommittee consisting of E. M. James, T. C. Smith, and J. R. Mays Jr., chairman. An overwhelming majority

of both the Refining and Uniform Methods Committee members approved this definition for adoption by the Society and submission to the Bureau of the Census. However there was minority opposition to it in both committees. For this reason, and because of our uncertainty concerning the use to which it might be applied, the Uniform Methods Committee requested authorization to inquire further of the Bureau of the Census regarding the purpose for which the definition is required, also authority to modify its phrasing as seemed advisable in the light of the information obtained. The final definition to be recommended to the Society must have the approval of the Refining and Uniform Methods Committees. This permission was granted.

At the 41st Annual Meeting in Atlanta, May 3, 1950, a brief report of this investigation was made. From the reply to our inquiry it was apparent to the Uniform Methods Committee that the desired definition must either be so comprehensive as to include all oils, or a multitude of definitions must be formulated to cover individual types and sources, with processing procedures which become extremely complex. The definition submitted by the Refining Committee