

viscous than ordinary phosphoric acid and may develop crystals on long storage in cold weather. It may be desirable, if practicable, to ammoniate the acid as it is received rather than to store it for long periods. When storage is required, care should be exercised to exclude water and moist air. Burying the storage tank or heating its contents may be desirable in cold climates.

The efficiency of centrifugal pumps with superphosphoric acid of 76% phosphorus pentoxide content at ordinary temperatures is low, and positive displacement pumps such as gear, lobe, or screw pumps would be more suitable. Weight tanks, tanks equipped with sight gages, positive displacement meters, magnetic flow meters, etc., may be used to measure the acid. However, with rotameters or orifice meters, which are sensitive to viscosity changes, the acid should be heated and kept at a constant temperature. Any general-purpose pump designed for pumping ordinary liquid fertilizers should be suitable for pumping the high-analysis liquids.

The production of high-analysis liquids

from superphosphoric acid offers advantages to the liquid fertilizer industry. Improved formulations, decreased storage and handling costs, and better distribution procedures for the products are possible with this material. The 11-33-0 grade contains 47% more plant nutrient per gallon than the 8-24-0 grade. The 11-33-0 liquid may be produced as the base solution in centrally located plants and distributed to mixing plants where potassium chloride and supplemental nitrogen may be added, thereby providing for more widespread distribution.

Greenhouse and field tests indicate that the crop response from liquids produced from superphosphoric acid has been equal to that obtained with standard fertilizer materials.

Superphosphoric acid is being used in the production of high-analysis liquids by several companies. The Tennessee Valley Authority has operated a small plant to produce high-analysis liquid fertilizers for demonstration purposes.

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FERTILIZER MATERIALS ANALYSIS

Colorimetric Determination of Aluminum in Acid Solutions of Phosphate Rock

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A procedure is presented to eliminate the interference of iron in the colorimetric determination of aluminum in acid solutions of phosphate rock. It involves extraction of the iron-cupferron complex with chloroform, leaving the aluminum in solution to be determined colorimetrically using Alizarin Red S as the color complex. Aluminum was determined in synthetic samples containing iron oxide-alumina ratios up to more than 7 to 1.

THE GRAVIMETRIC (Glaser) method (1, 5) commonly used for the determination of aluminum in phosphate rock is time-consuming and subject to serious error. Wide variations in the results obtained by this method by different analysts on identical samples of phosphate rock are cited by Barton (3), who states, "The alumina results reported on monthly check samples seldom vary by less than 40% between the maximum and minimum values and occasionally vary by as much as 200%." The chief source of error is the coprecipitation and retention of phosphate in excess of the iron and aluminum phosphates. The hydrolysis of these salts when washed

with water or a solution of an electrolyte like ammonium nitrate makes it difficult, if not impossible, to judge by a test for phosphate when the excess phosphate has been removed (5, p. 505).

In view of these disadvantages a reliable colorimetric method was sought, based on the sodium alizarin sulfonate (Alizarin Red S) procedure proposed by Atack (2). According to Yoe and Hill (10), calcium and phosphate do not interfere in this procedure, but iron and fluorine do. Iron is the more troublesome of the two, because fluorine is easily eliminated by evaporation of the test solution to fumes with sulfuric acid (3). Barton (3) found that aluminum

can be best determined at a wave length of 370 m μ in the presence of iron, if the test sample does not contain more than 0.05 mg. of iron oxide with a like amount of alumina.

The procedure here described is based on colorimetric determination of aluminum in an acid solution of phosphate rock after the iron has been separated by solvent extraction of the cupferron-iron complex with chloroform (7-9). Vanadium is extracted along with the iron (7). Tests with synthetic mixtures showed that chromium at the concentrations occurring in most western rocks does not interfere with the aluminum determination. Alumina in synthetic

mixtures having iron oxide-alumina ratios up to more than 7 to 1 has been accurately determined by this procedure. Other organic solvents, such as carbon tetrachloride (8) or a mixture of benzene and ether (7), have been used to extract the iron complex. Cupferron precipitates iron in a strong acid medium, leaving aluminum in solution (4; 5, p. 116). The filtration method for separating the two elements is not suitable because of the interference of excess cupferron with the subsequent colorimetric determination of aluminum.

Procedure

Phosphate Rock Digestion. To a 1-gram sample of rock in a 250-ml. Erlenmeyer flask add 10 ml. of concentrated hydrochloric acid and 5 ml. of concentrated nitric acid, and digest on the hot plate until the red fumes of nitric acid disappear. Cool and add 10 ml. of concentrated hydrochloric acid and about 50 ml. of distilled water. Heat to dissolve the salts, cool, transfer the solution to a 250-ml. volumetric flask, and make up to volume. After mixing, allow the acid-insoluble residue to settle out, or filter a portion of the solution through a dry (No. 41 Whatman) filter paper into a dry container.

If the sample is wet-process phosphoric acid, transfer a suitable sample to a 250-ml. Erlenmeyer flask and proceed as in the digestion of phosphate rock.

Extraction of Iron. Transfer a 15-ml. aliquot of the above solution to a 125-ml. separatory funnel. (If the sample contains less than 0.50% or more than 2.0% of alumina, increase the volume of the aliquot to 25 ml. or reduce it to 10 ml., respectively.) Add 5 ml. of 2*N* hydrochloric acid and 2 ml. of a freshly prepared 6% aqueous solution of cupferron. A reddish brown precipitate is formed. Add 10 ml. of chloroform and shake vigorously for about 45 seconds. Allow the layers to separate, draw off the organic solution, and wash the aqueous phase with 5 ml.

of chloroform. Test for the complete removal of iron by adding a few drops of cupferron solution. Iron is completely removed when a drop of the reagent forms a transient white precipitate. Remove the excess cupferron by washing the aqueous solution with 10 ml. of chloroform. Drain the aqueous solution into a 100-ml. volumetric flask, rinse the funnel with water, make up to volume, and mix thoroughly.

Determination of Aluminum. Transfer a 10-ml. aliquot of the iron-free solution to a 150-ml. beaker, add 0.5 ml. of

Table I. Aluminum Recovered from Synthetic Mixtures

Al ₂ O ₃ , %		Std. Dev.	Coeff. of Variation, %
Added	Found ^a		
0.33	0.31	0.030	9.55
0.50	0.53	0.057	10.80
0.66	0.65	0.029	4.42
1.00	1.03	0.033	3.20
1.33	1.38	0.044	3.19
1.50	1.49	0.028	1.88
2.00	1.98	0.050	2.53

^a Average of six replicates.

Table II. Comparison of Results Obtained by Colorimetric and Gravimetric Procedures

Sample No.	Source and Type of Rock	Colorimetric				
		Gravimetric ^a		% Al ₂ O ₃		
		% Fe ₂ O ₃	% Al ₂ O ₃	Iron present	Iron extracted	Std. dev.
3300 ^b	Florida land pebble	1.23	1.09 ^c	1.35	1.05	0.02
439	Florida land pebble	1.90	1.01	1.55	1.10	0.06
618	Florida land pebble	1.51	0.89	1.35	1.00	0.04
910	Florida land pebble	2.59	1.11	1.78	1.12	0.02
908	Tennessee brown rock	2.52	1.16	1.43	1.11	0.10
762	Tennessee brown rock	2.25	1.78	1.85	1.63	0.03

^a With the exception of sample 3300, figures for Fe₂O₃ and Al₂O₃ are taken from Tables 3 and 4 (5).

^b Check sample 15, Assoc. Florida Phosphate Mining Chemists.

^c Statistical average of results obtained by 20 different analysts. Minimum 0.79%, maximum 1.45%, numerical average 1.11% Al₂O₃.

1 to 1 sulfuric acid, and evaporate to fumes of sulfur trioxide. Cool and wash the contents into a 100-ml. volumetric flask with about 40 ml. of water. Add 3 ml. of 0.1% Alizarin Red S indicator solution, 10 ml. of 3*N* ammonium hydroxide, and 5 ml. of 5*N* acetic acid. Dilute to volume, mix thoroughly, and read the per cent transmittance in the range, 350 to 400 mμ (Figure 1). Read the amount of aluminum (Al₂O₃) in the sample from a previously prepared calibration curve or calculate it from an equation for the calibration data. Run a blank with each group of samples (only an occasional check with a standard is necessary).

Discussion

The data presented here were obtained with an Evelyn photoelectric macrocolorimeter. Figure 1 compares the absorbance curves of a standard aluminum solution and a blank, obtained with this instrument, over a wide spectral range. The maximum absorbance difference occurs in the range 350 to 420 mμ which corresponds closely with the transmittance limits for filter 375. A linear relation was found over an alumina concentration range of 0.0 to 0.10 mg. per test solution.

A series of synthetic solutions, equivalent to a 1-gram sample of phosphate rock dissolved and diluted to 250 ml., was prepared to determine the efficiency of the recovery of alumina by the extraction procedure. Each mixture contained ferric chloride equivalent to 2.5%

Table III. Aluminum Content of Wet-Process Phosphoric Acid

P ₂ O ₅ , %	Fe ₂ O ₃ , %	Al ₂ O ₃ , %		
		1	2	Difference
31.4	0.88	1.68	1.66	0.02
34.0	0.97	1.59	1.57	0.02
32.5	1.14	1.68	1.71	0.03
32.3	1.16	1.70	1.65	0.05
32.5	1.06	1.80	1.83	0.03

Fe₂O₃, and calcium phosphate equivalent to 33.0% P₂O₅ and 46.0% CaO. The alumina equivalent of the added standard aluminum (NBS standard sample 44c) varied from 0.33 to 2.0%. The iron was extracted and the alumina was determined in accordance with the indicated procedure. The results obtained in 42 determinations on seven test samples are shown in Table I.

In Table II the results for alumina obtained colorimetrically on six phosphate rocks with and without removal of iron are compared with the gravimetric results of other investigators (6). When the determination was made without extracting the iron (column 5), the results for alumina were high. The results for alumina after the iron had been extracted (column 6) are of the same order of magnitude as obtained by the longer and more tedious gravimetric procedure. Standard deviations (column 7) of four colorimetric determinations of alumina (column 6) show much less variation than those cited by Barton (3) on the gravimetric results of

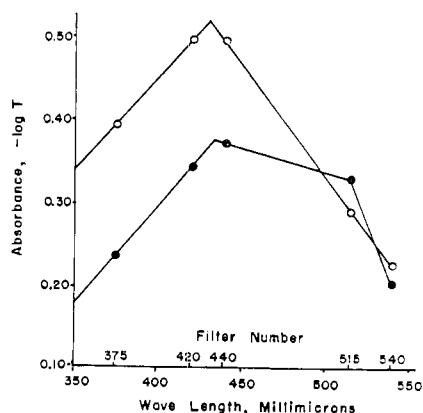


Figure 1. Absorbance curves with Alizarin Red S

● 0.10 mg. of Al₂O₃
○ Blank

monthly check samples (cf. footnote,° Table II).

The application of the procedure for the determination of aluminum in wet-process phosphoric acid is shown in Table III. Duplicate determinations differed by 0.05% or less.

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WHISKEY AGING

Effects of Barreling Proof on the Aging of American Whiskeys

Three whiskey distillates were barreled for aging at 110 (control) and distillation proof. Experimental barreling proofs were 118, 127, and 154. During 8-year aging in new charred oak barrels the percentage losses of whiskeys barreled at proofs above 110 were slightly lower than the controls; the tendency was not statistically significant because of the relatively small number of experimental barrels. Chemical characteristics developed during aging of whiskeys barreled at 118 and 127 proofs fell within normal limits, but at 154 proof were lower than normal. Flavor after aging 8 years was normal in the whiskey barreled at 118 proof, slightly less mature at 127 proof and different at 154 proof because of a spicy green oak taste. An industry-wide experiment is now under way.

TRADITIONALLY, American distillers have barreled their whiskey distillates for aging at potable proof—i.e., about 100 to 102 proof (50 to 51% alcohol by volume). In other countries, distilled spirits are barreled for aging at proofs from 124 to 150 and more (4, 12).

In 1898, 31 U. S. distillers barreled their whiskeys between 100 and 104 proof (3); in 1929, 11 distilleries barreled their whiskeys between 100 and 102.6 proof (13), and in 1945, 13 distillers cooperating in an aging experiment barreled 16 whiskey distillates at proofs ranging from 101.1 to 110.0 (8).

Government regulations define straight whiskey as an alcoholic distillate from a fermented mash of grain distilled at not over 160 proof, barreled at not less than 80 nor more than 110 proof, and aged for not less than 24 months in charred new oak barrels (10, 17).

In the past, the barreling proof limitation on U. S. whiskeys was of little concern, but in recent years it has taken on greater importance. There are several obvious economic advantages in barreling whiskey at proofs higher than 110, if whiskey quality is not impaired

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and losses during aging are not excessive. These advantages have become increasingly pertinent recently because of the increasing high costs of new quarter-sawn white oak cooperage and warehouse aging facilities.

If whiskeys could be aged at higher proofs, more proof gallons per barrel would result and the number of proof gallons stored per warehouse would be increased. For example, a 50-gallon barrel filled with 102-proof whiskey contains 51 proof gallons. At 110 proof it would contain 55 proof gallons and at 130 proof, 65 proof gallons, resulting in gains of 7.8 and 27.4%, respectively. Very few U. S. whiskeys are distilled above 130 proof.

There have been no data published on the effects of aging U. S. whiskeys barreled at proofs above 110 on the losses experienced or the chemical and organoleptic quality. The data summarized below give the results of three typical experiments taken from a more extensive study on this subject, started in 1949 and concluded after an 8-year aging period.

Experimental

Distillates. Each experiment con-

sisted of a typical whiskey distillate barreled at two proofs: 110 proof (control) and distillation proof. It had been established previously that barreling proofs of 102 and 110 give whiskeys of comparable quality after aging. Ever since 1944, the company's standard barreling proof has been 110 for American whiskeys.

The three distillates chosen for this report represent whiskeys distilled at high, low, and medium proofs: rye I, 154 proof; bourbon II, 118 proof; bourbon III, 127 proof. These distillates were from normal routine, full-scale commercial productions.

Cooperage. The barrels came from three carloads of routine receipts. Both experimental and control barrels for a single whiskey type came from a single carload of barrels. All barrels were charred new white oak barrels of approximately 50-gallon capacity, manufactured by the Hiram Walker Cooperage Division in accordance with the company's specifications. For each whiskey at each barreling proof, five barrels were chosen at random for the studies.

Warehousing. Experimental barrels were racked alternately with control barrels in a location considered normal