distilled water. The copper-on-silica gel catalyst (B, Table I) was separated from the pale blue supernatant by filtration and dried at 110 C to yield 3.04 g. Analysis by atomic absorption (3) showed that this catalyst contained 15% copper. A copper-on-silica gel catalyst was similarly prepared with copper sulfate (Catalyst A, Table I) except the catalyst was thoroughly washed with distilled water to ensure complete removal of sulfate ions.

A 20% copper-on-silica gel catalyst (C, Table I) was prepared as follows: Enough 30% ammonium hydroxide (3.6 ml) was added to 3 g copper sulfate pentahydrate in 15 ml water to redissolve the copper hydroxide. About 2.5 g of silica gel was added. The volume was then gradually made up while swirling the flask to 1 liter with distilled water. Catalyst C was separated from the blue supernatant by filtration, washed thoroughly with distilled water and dried at 110 C to yield 3.3 g. Analysis by atomic absorption (3) indicated that Catalyst C contained 20% copper.

After these catalysts were calcined at 350 C for 2 hr, they were evaluated for the selective hydrogenation of soybean oil (Table I). Hydrogenation procedure and methods of analysis were the same as described previously (1,2). All catalysts at a concentration of 0.1% as copper oxide are much more active than 0.5% commercial copper-chromite catalysts (4) under similar conditions of temperature and pressure. The activity and reuse properties of these catalysts compare favorably with the chemisorbed catalyst (2). The activity of catalysts prepared from copper sulfate was somewhat diminished during third reuse. No significant differences in the amount of *trans* isomers were found. In general the selectivity ratios obtained with these catalysts are lower than those obtained with the previously reported catalyst (2); after an IV drop of 13-14 units the amount of linolenate in the product was 0.9-1.7% with the present catalysts while it was below 1% with chemisorbed catalyst (2). Selectivity for the reduction of linolenate decreased during reuse possibly due to poisoning of the catalyst. The selectivity ratios of 8-12 achieved with the present catalysts compare favorably with those obtained with commercial copper-chromite catalysts (4).

SAMBASIVARAO KORITALA
Northern Regional Research Laboratory[1]
Peoria, Illinois 61604

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Atomic absorption analyses were performed by G. List.

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[1]No. Mark. and Nutr. Res. Div., ARS, USDA.

Trace Phosphate Analysis in Silicate-Containing Detergents

ABSTRACT

A colorimetric method has been developed, suitable for determining low levels (10-200 ppm) of phosphorous in detergent formulations containing large amounts of silicate. Samples are ashed to remove organic matter, hydrolyzed to convert all phosphates to ortho-phosphate, and centrifuged to remove any SiO_2, carbon or other solids. Phosphomolybdic acid is formed and extracted into an organic solvent, where it is reduced to the classic molybdenum blue color by stannous chloride. The procedure yields accurate and reproducible results, with reliability at the 25 ppm phosphorous level of ±3 ppm.

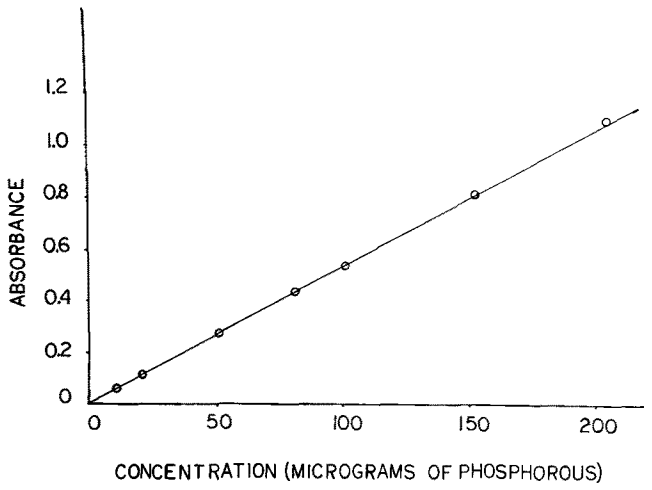

FIG. 1. Calibration curve; phosphorous concentration vs. absorbance.

Interference problems, inherent in analyzing current detergent formulations by existing standard methods, have been pinpointed (1,2). We have developed a simple colorimetric method capable of analyzing silicate-containing detergents for phosphate, at the 10-200 ppm level of phosphorous. The method is based, after ashing and removal of silicate, on the formation of phosphomolybdic acid, which is extracted into benzene-isobutanol and reduced to molybdenum blue by stannous chloride. The method as written calls for sample sizes of 1 g. If lower limits of phosphate detection are required, larger sample sizes may be used. The procedure is as follows: A 1.00 g sample is placed in a porcelain crucible and ashed overnight in a muffle furnace at 450-650 C. If any carbon remains, it will be removed in a later step. The cooled residue is transferred, with the aid of 40 ml of water and 8 ml of 8 N sulfuric acid, to a 250 ml beaker, and heated on a steam bath for 1 hr. Beakers are not covered. The final volume, after heating, will be about 20 ml. The hydrolyzed sample is transferred to a 40 ml centrifuge tube using several small portions of water to assist in the transfer. The sample is centrifuged at about 2000 rpm for ten min, or until all solids settle to the bottom of the tube. This centrifugation effectively removes silicate, now present as SiO_2, and any carbon which may have remained from the ashing. The clear solution is carefully decanted into a 100 ml extraction cylinder. It is not necessary to wash the precipitate. The solution is diluted with water to 48 ml, and 50 ml of benzene-isobutanol 1:1, followed by 8 ml of 10% ammonium molybdate solution, is added. The stoppered cylinder is shaken vigorously for a minimum of 15 sec to extract the

TABLE I

Summary of Replicate Detergent Analyses

Sample	"As is" detergent, ppm of P found	Detergent samples, each fortified with 15 ppm of P ppm of P found
1	12	31
2	11	28
3	13	25
4	13	25
5	13	26
Average ± average deviation	12.4 ± 0.7	27.0 ± 2.0

TABLE II

Recovery of Phosphate From Fortified Detergent Samples

Sample no.	Amount of phosphate added, ppm as P	Total P found, ppm	Added P recovered, ppm[a]	Per cent recovery
1	15	31	18.6	124
2	15	28	15.6	104
3	15	25	12.6	84
4	15	25	12.6	84
5	15	26	13.6	91
Average	15	27.0	14.6	97.5

[a]Determined by subtracting initial phosphorus content of 12.4 ppm from total P found.

phosphomolybdic acid into the upper organic phase. A 25 ml aliquot of the separated organic phase is transferred to a 50 ml volumetric flask. A 20 ml portion of 2% H_2SO_4 in methanol is added, followed by 1 ml of stannous chloride, prepared by dissolving 10 g of stannous chloride in 25 ml of concentrated HCl and diluting 0.5 ml of this solution to 100 ml with water. This diluted solution must be prepared fresh each day. After mixing, the solution is diluted to the mark with methanol. Color development is allowed to proceed for a 10 min period and then absorbance is measured at 650 nm, using 1 cm cells. Samples are not allowed to stand more than 30 min. The concentration of phosphorous is determined directly from a standard curve, prepared by taking known amounts of an ortho-phosphate solution, transferring them to extraction cylinders, diluting to 48 ml, continuing as described above, and plotting phosphorous concentration against absorbance. The standard curve will obey Beer's law between concentrations of 10-200 μg of phosphorous (Fig. 1).

Using the above procedure, a group of five 1 g samples taken from the same carton of a silicate-containing, "phosphate free" detergent were analyzed. Additionally a second group of five 1 g samples from the same carton were taken, and each fortified with phosphate equivalent to 15 ppm as phosphorous, prior to the ashing step. The reproducibility of the method, in terms of the amount of phosphorous found in each of the samples, is shown in Table I. Table II shows the amount of phosphate recovered from fortified samples of detergent. A statistical analysis of the data indicates reliability of low level assays to be ±13%, with the average percentage recovery of replicate samples of phosphate being 98.5%. The reliability of an assay for a sample containing 25 ppm of phosphorous would be ±3 ppm.

I.I. DOMSKY
M.B. GRABER
M.M. GOLDSTEIN
Research and Development Department
Armour-Dial, Inc.
Chicago, Illinois 60608

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Grapefruit Seed Oil Sterols

ABSTRACT

Grapefruit seed oil sterols separated from other lipids by Florisil column chromatography were characterized by gas liquid chromatography. The presence of stigmasterol, campesterol and β-sitosterol is indicated. Expressed in terms of peak area, the three sterols are present in proportions of 2.5%, 7.4% and 90.1% of the total, respectively.

Seeds of citrus fruits contain about 30% oil (1). While the proportion of seed to fruit is relatively small, there is considerable potential of citrus seed oil as a by-product of fruit processing. Processing and refining methods have been developed for the commercial production of citrus seed oils (1,2). Certain characteristics of grapefruit seed oils have been published (3-5). While the identification of sterols in other portions of citrus fruit has been reported (5-7), there is a lack of information regarding seed oil sterols. This investigation reports the nature of sterols in grapefruit seed oil as characterized by gas liquid chromatography (GLC).

Seeds were obtained from grapefruit, *Citrus paradisi* (Macf.), representing two varieties: Yuma pink and Yuma yellow. The seeds were removed from the fruit, washed with distilled water, air-dried and extracted in a high speed mixing blender with chloroform-methanol 1:1 v/v (8). The