LETTER TO THE EDITOR

Measurement of Low Levels of Phosphate in Detergents[1]

Sir: A recent letter (JAOCS 48:144, 1971) described the interference from silicates and borates with the standard titrimetric procedure for phosphates in detergents, as found in AOCS Method Da 20b-57 or ASTM Method D 820-58. Procedures were given in the above letter which eliminate these interferences when significant amounts of phosphate are present. Neither the standard nor the modified method gives correct results when a few per cent or less phosphate is present.

Data obtained when AOCS Da 20b-57 was applied to laboratory-prepared samples of detergent powders containing sodium silicate and other builders along with known low levels of sodium tripolyphosphate (STP) are shown in column two of Table I. The percentage of STP present, calculated as per cent of P_2O_5 from the level of STP added, is shown in column one. Correct results on these samples obtained using standard emission and X-ray fluorescence spectroscopy techniques are shown for comparison.

Table II shows data for some currently available commercial detergent products manufactured without added phosphate; results by AOCS Da 20b-57 in column one are significantly higher than those obtained by emission spectroscopy shown in column two. X-ray fluorescence data were not obtained on these samples. Several modifications of the standard procedure including those mentioned in the references cited above were used, but none was found to analyze correctly these samples.

At a time when detergent phosphate levels are of intense interest it is important that standard methods give correct values. A method valid at low phosphate levels is most necessary, particularly since procedures will be needed to judge compliance with certain legislation involving phosphate levels in detergents. Emission and X-ray fluorescence spectroscopy, while capable of accurately and precisely measuring low levels of detergent phosphate, are not convenient for routine or control use particularly by a small laboratory.

Numerous procedures may be found in the literature for analysis of phosphates; in our laboratory we are using a colorimetric procedure based upon the so-called "Single Solution" version of the molybdenum blue method for phosphate described by Murphy and Riley in 1962 (Anal. Chim. Acta 27:31, 1962). We considered a number of other procedures such as the one described by Martin and Doty (Anal. Chem. 21:965, 1949) or its more recent modifications, or the automated procedure for detergent phosphates published by Lundgren (Anal. Chem. 32:924, 1960). Our final choice of the Murphy and Riley approach was based upon an overall consideration of simplicity in equipment and operation, precision, accuracy and lack of interferences. Addition of an isobutyl alcohol extraction step to the Murphy and Riley procedure, as found in the Martin and Doty procedure and others, serves to eliminate interference caused by solution turbidity or product colorants. Our procedure, which we recommend to those measuring low levels of phosphate in detergents, is described below. We have found no interferences from components commonly present in detergents, including silicate which is a common interference in molybdenum blue procedures. Results obtained using the proposed procedure are shown in the last column of Tables I and II. Results show good agreement with spectroscopic data and, in the case of the samples in Table I, the levels known to be present. The low levels of phosphate found in the products manufactured without added phosphate, as shown in Table II, are real and may represent phosphate introduced as contaminant in raw materials or equipment. The procedure is quite suitable for high levels of phosphate as well. The data shown here were chosen to demonstrate low level phosphate applications where the standard or modified titrimetric procedures do not apply. We have measured the standard deviation of the procedure as ± 0.35% in the 20-30% P_2O_5 range and ± 0.02% in the 0-2% P_2O_5 range.

EXPERIMENTAL PROCEDURE

Analytical reagent grade chemicals and standard analytical techniques are used throughout.

The Single Solution Molybdate Reagent is prepared from solutions of sulfuric acid, ammonium molybdate, potassium antimonyltartrate and ascorbic acid as follows: Solution A: cautiously add 140 ml of concentrated sulfuric acid to 900 ml distilled water. Solution B: dissolve 15.0 g ammonium molybdate in 500 ml distilled water; store in the dark. Solution C: dissolve 13.5 g ascorbic acid in 250 ml distilled water; store in a refrigerator; discard in one week. Solution D: dissolve 0.35 g potassium antimonyltartrate in 500 ml distilled water.

Mix thoroughly 125 ml Solution A, 50 ml Solution B, 50 ml Solution C, and 25 ml Solution D. The resulting Single Solution Molybdate Reagent should be yellow in color. A greenish or blue color indicates phosphate contam-

TABLE I

Measured Per Cent of P_2O_5 in Laboratory Prepared Low-Phosphate Detergents

		Per cent of P_2O_5 found			
Sample	% P_2O_5 present	AOCS Da 20b-57	X-Ray fluorescence	Emission spectroscopy	Proposed colorimetric
1	None	.63	.00	.00	.00
2	.11	.85	Not analyzed	.11	.11
3	.23	.98	.25	.23	.23
4	.34	1.10	.41	.32	.32
5	.80	1.58	.73	.87	.76
6	1.72	2.40	1.74	2.06	1.65

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[1] Presented at the AOCS Meeting, Houston, May 1971.

TABLE II

Measured Per Cent of P_2O_5 in Commercial Low-Phosphate Detergents

	Per cent of P_2O_5 found		
Sample	AOCS Da 20b-57	Emission spectroscopy	Proposed colorimetric
A	.53	None found	.05
B	.95	None found	.03
C	.63	None found	.02
D	1.9	.1	.15
E	.75	None found	.01
F	.98	None found	.00
G	.87	None found	.03

ination, in which case the solution should be discarded. The Single Solution Molybdate Reagent must be prepared fresh daily.

A phosphate stock solution for calibration may be prepared by dissolving in a 1000 ml volumetric flask 0.5000 ± 0.0005 g of reagent grade disodium hydrogen phosphate (anhydrous) which has been previously dried at 105 C for 1 hr. This stock solution contains ortho phosphate equivalent to 250 μg P_2O_5/ml. Aliquots of a quantitative dilution of the phosphate stock solution containing ortho phosphate equivalent to 25-140 μg of P_2O_5 are transferred to 250 ml separatory funnels. Distilled water is added to each separatory funnel with a graduated cylinder to make a total volume of 100 ml. One hundred milliliters of distilled water is used as a blank. Twenty milliliters of Single Solution Molybdate Reagent is added to each calibration solution; the separatory funnel is stoppered and shaken for 1 min. After standing for 10 min, 40 ml of isobutyl alcohol is added, the solution shaken vigorously for 60 sec and the solution allowed to stand for 5 min. The bottom, aqueous layer is discarded. The extracted molybdenum blue complex is drained into a 50 ml volumetric flask. The separatory funnel is washed with about 5 ml ethyl alcohol. The washings are added to the extract and the extract diluted to volume with ethyl alcohol. The extract absorbance is determined at 690 nm and a calibration plot of micrograms P_2O_5 vs. absorbance prepared.

Samples are determined by dissolving an appropriate representative sample of detergent powder, usually 5-10 g, in 500 ml distilled water in a 1000 ml volumetric flask. Fifty milliliters of concentrated sulfuric acid are cautiously added and the flask is placed on an open steam bath for 1 hr (or more, if desired) to convert all phosphate to the ortho form. The sample solution is cooled and brought to volume with distilled water. An aliquot of the hydrolyzed sample solution (or a quantitative dilution of that solution) containing ortho phosphate equivalent to 40-100 μg of P_2O_5 is transferred to a separatory funnel. Distilled water is added to a total volume of 100 ml and excess acid neutralized by addition of 2 N sodium hydroxide to the phenolphthalein endpoint. The molybdenum blue complex is formed, extracted, and the absorbance determined as described above for calibration solutions.

The percentage P_2O_5 present in the original sample is calculated from the weight of sample taken, dilutions used, and the micrograms of P_2O_5 in the aliquot of sample solution (or its dilution) used.

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