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A Modified Procedure for the Determination of Phosphorus in Detergents

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ENVIRONMENTAL PROTECTION SERVICE

A MODIFIED PROCEDURE FOR THE DETERMINATION OF PHOSPHORUS IN DETERGENTS

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ABSTRACT

The procedure described by the American Society for Testing and Materials for the determination of phosphorus in detergents has been studied. It is concluded that, at 5% phosphorus as P_2O_5, the method as written does not give a true measure of the phosphorus level. A modified titrimetric procedure has been developed which overcomes the difficulties experienced in the ASTM procedure at low phosphorus levels.

RESUME

On a étudié la méthode de dosage du phosphore contenu dans les détergents que décrit l'American Society for Testing and Materials. On a trouvé qu'à une concentration (exprimée en P_2O_5) de 5 p. 100 en phosphore, cette méthode ne donne pas une mesure vraie de la concentration en phosphore. On a donc élaboré une méthode de titrage modifiée qui surmonte les difficultés que présente la méthode de l'ASTM aux faibles concentrations en phosphore.

CONTENTS

1 INTRODUCTION

Regulations made under the Canada Water Act limit the amount of phosphorus that can be present in laundry detergents made in or imported into Canada. From 1st August, 1970 to December 31, 1972, the regulation specified the maximum permissible concentration as 20% expressed as phosphorus pentoxide (P_2O_5). Since January 1st, 1973 the maximum permissible concentration has been 5% P_2O_5. The regulations further decree that the method of analysis shall be that prescribed from time to time by the American Society for Testing and Materials.

In earlier work (1) using ASTM Method D820-58 (Reapproved 1965) it was found necessary to add a specific step for removal of borate interference, and with this modification the method was found to be satisfactory for analysis of detergents against the "20% P_2O_5 limit". The latest ASTM Method published (ASTM D820-72) (2) is more specific in its description of silicate-dehydration and contains a step for borate removal. However at low phosphate levels (5% P_2O_5) some problems have been experienced, both in the Environmental Protection Service and Water Quality laboratories, in obtaining reproducible results with the method. This seems to be recognized in the ASTM write-up, which states "This method does not apply when the level of phosphate present in equivalent to or less than 2 percent P_2O_5". From a study of the method, it was concluded that two problems exist in the ASTM procedure: 1) In the presence of the electrolyte from the detergent and the digestion-neutralization procedure, titration between two fixed pH's does not give a valid measure of the normality of a weak-acid solution; and, 2) There is potential interference from carbonate carried in with the sodium hydroxide.

This study concluded that the ASTM procedure as written is not a satisfactory method for the analysis of phosphorus in detergents at the 5% P_2O_5 level.

2 BACKGROUND

The determination of phosphates in a detergent as described in ASTM D820-72, involves the conversion of the phosphates to orthophosphate by boiling with hydrochloric acid. The orthophosphate is then determined by a "weak-acid" titration between the pH's of 4.3 and 8.8. However, it was found that the presence of an added electrolyte (e.g. NaCl) changes the shape of the pH-titration curve obtained when a solution of orthophosphate is titrated with sodium hydroxide solution. This is shown in Figure 9, where the pH-titration curves of KH_2PO_4 solution titrated with NaOH solution alone and in the presence of NaCl at three concentrations have been plotted. Similar results were seen with Na_2SO_4. It is apparent that, except in the absence of added electrolyte, the points of inflexion of the titration curves do not correspond to the two pH's given in the ASTM method and marked in Figure 1. Shown in Figures 2 - 5 are the titration curves for 4 detergents. Figure 6 shows a phosphate standard solution, analysed by the modified procedure described below. From Figures 1 - 6 it is evident that the only satisfactory way to determine the end-points in the titrations is to plot a titration curve for each determination. The points of inflexion may best be determined by plotting Δ pH against volume of titrant added (figures 7 & 8).

The determination of orthophosphate is affected by other weak acids such as silicates, borates, carbonates etc., and these materials, which enter with the detergent, are removed in the procedure. However, the hydrochloric acid used to hydrolyze the phosphates must be neutralized with concentrated sodium hydroxide. Absolutely carbonate-free sodium hydroxide is difficult to prepare (the procedure being to decant the clear 50% sodium hydroxide from settled carbonate (D820-72)) and requires special precaution to prevent subsequent adsorption of CO_2 from the atmosphere. The carbonate which may enter with sodium hydroxide is determined as phosphate in the ASTM procedure and, at low levels of phosphate, can significantly distort the results obtained. The procedure below overcomes this possible interference and essentially calibrates the phosphate determination and all the reagents.

3 REAGENTS

3.1 Sodium Hydroxide - approximately 0.25N (not standardized) - prepared from carbonate free 1 + 1 sodium hydroxide by dilution.

3.2 Sodium Hydroxide Solution (1 + 1) - Dissolve sodium hydroxide (NaOH) in an equal weight of water. When using, decant the solution from the settled carbonate. A more dilute solution may be used. NaOH solutions must be protected from carbon dioxide (CO_2) contamination.

3.3 Potassium dihydrogen phosphate - reagent grade oven-dried at 105°C.

3.4 Hydrochloric Acid - reagent grade, specific gravity 1.19.

3.5 Methanol, at least 90% CH_3OH.

4 PROCEDURE

4.1 Weigh out 2.5 ± 0.1 g detergent to the nearest 0.001 g Record weight (w).

4.2 Transfer the sample to a 250 ml Pyrex 'Berzelius' type beaker. Place the beaker in a cold muffle furnace. Heat the sample to 550°C and leave at this temperature for 30 minutes. Cool to room temperature and cautiously add 10 ml of Hydrochloric Acid. Cover with a Fisher "Speedyvap" watch glass and evaporate to dryness. Cool and repeat the HCl addition and evaporation two additional times. After the third evaporation, continue to heat for a further 20 minutes to ensure complete dehydration of SiO_2. Cool and proceed with section 4.4 if it is known that the sample does not contain Borate or Perborate.

4.3 If Borate or Perborate are suspected in the sample, prepare a solution of 90 ml Methanol and 10 ml Hydrochloric acid. Add 10 ml of this solution to the sample, heat the sample on a shaker hot plate or steam bath and ignite the methanol vapour. If the vapour burns with a green flame, borate is present and must be removed before proceeding. If no green flame is observed, evaporate to dryness and proceed with section 4.4. To remove borate and perborate add to the sample 200 ml methanol, 10 ml Hydrochloric acid, and 3 or 4 hollow glass beads. Cover the beaker with a watch glass (Fisher "Speedyvap") and boil down to

20 ml on a steam bath. (The boiling time must be at least 30 minutes). Evaporate down to less than 10 ml on a steam bath under a stream of nitrogen or clean dry air.

4.4 Add 90 ml of deionized water and 10 ml Hydrochloric acid (by pipette) to the sample. Cover with a watch glass and boil gently for 30-60 minutes. All phosphate must be in the ortho form. Cool to room temperature.

4.5 Dilute to 200 ml, place on an electrometric titration stand and neutralize to pH of about 3.0 with 1 + 1 NaOH added from a burette, (a polyproplyene burette is found to be satisfactory). Record the volume of 1 + 1 NaOH used (v). As necessary cool the beaker during this neutralization to maintain temperature below $30^{o}C$.

4.6 Add the 0.25N NaOH in 0.25 ml increments, recording the pH and volume added after each addition. Plot the pH change (ΔpH) against volume of NaOH titrant added, and determine the titre between the two end points (T). Two typical curves are shown in Figures 7 and 8, which illustrate this procedure.

4.7 If a number of detergents are being run at the same time calculate the mean volume of 1 + 1 NaOH added to them (V mean).

4.8 To calibrate the 0.25N NaOH and other reagents; weigh out 0.24 ± 0.01 g KH_2PO_4 to the nearest 0.0001 g, place in a 250 ml beaker, add 200 ml water, add 8 ml Hydrochloric acid and boil gently for 30 minutes. Cool to room temperature and add the mean volume of 1 + 1 NaOH (V mean) used to neutralize the detergents. Cool and place on an electrometric titration stand and bring to a pH of about 3.0 with concentrated HCl. Carry out this procedure in duplicate.

4.9 Proceed as in 4.6 with each of the duplicates from 4.8 and calculate the mean titre for a weight of KH_2PO_4 of exactly 0.240 g. Record as T^{11}.

5 CALCULATION

$$P_2O_5 \text{ present} = \frac{T}{T^{11}} \times \frac{0.24}{W} \times 52.17\%$$

6 PRECISION AND ACCURACY

6.1 Nine detergent samples assaying from 3.3% to 4.7% P_2O_5 were analyzed in quadruplicate by the procedure. The results are shown in Table 1 (see appendix). The pooled standard deviation was 0.10% P_2O_5 and the pooled coefficient of variation was 2.5%

6.2 The phosphorus content of the above nine detergents was determined by taking the "titration solution" after the procedure as described above, diluting to 500 ml and measuring the phosphate content by an automated molybdenum-blue colorimetric method similar to that previously described (1). The manifold used is shown in Figure 9. Each solution was analyzed in duplicate, the results are also shown in Table 1. The pooled standard deviation was 0.08% P_2O_5 and the pooled coefficient of variation was 2.0%.

6.3 The difference between the results by these two methods was an average of 0.10% P_2O_5, the titration procedure giving the higher result. Treating the 18 mean results by the two methods as paired observations, the standard error of the mean difference was calculated. This calculation shows that the above difference of 0.10% P_2O_5 is a statistically significant difference at the 95% confidence level. It is believed that the colorimetric determination is a better measurement of the 'true' phosphorus content of the detergent and hence that there is a bias of approximately -0.10% P_2O_5 in the titrimetric determination. However in view of the standard deviation of 0.10% P_2O_5 in the titrimetric procedure based on the quadruplicate determinations, the 'true' result is included in the confidence limits of the result obtained by the titrimetric procedure.

6.4 The phosphorus content of the detergents was determined in quadruplicate by the ASTM procedure as written. These results are shown in Table 1. In all cases the ASTM procedure produces a result

that is higher than the 'true' value.

7 CONCLUSIONS & RECOMMENDATIONS

7.1 The titrimetric procedure described above gives a satisfactory measure of the phosphorus content of detergents at the 5% P_2O_5 level. The procedure is time consuming but it can be carried out using a minimum of equipment. The equipment required is that normally found in a small chemical laboratory.

7.2 A somewhat more precise and accurate determination can be carried out by the use of an automated colorimetric method, however, the necessary equipment is relatively expensive. For this reason it is recommended that the titrimetric procedure be used as the standard method for the determination of phosphorus in detergents.

REFERENCES

(1) P.D. Goulden, W.J. Traversy and M. Comba, "The Determination of the Phosphorus Content of Detergents". Tech. Bull No. 45, Dept. of the Environment, Canada, (1971).

(2) American Society of Testing and Materials, Book of Standards, Part 22, 144-146, (1972).

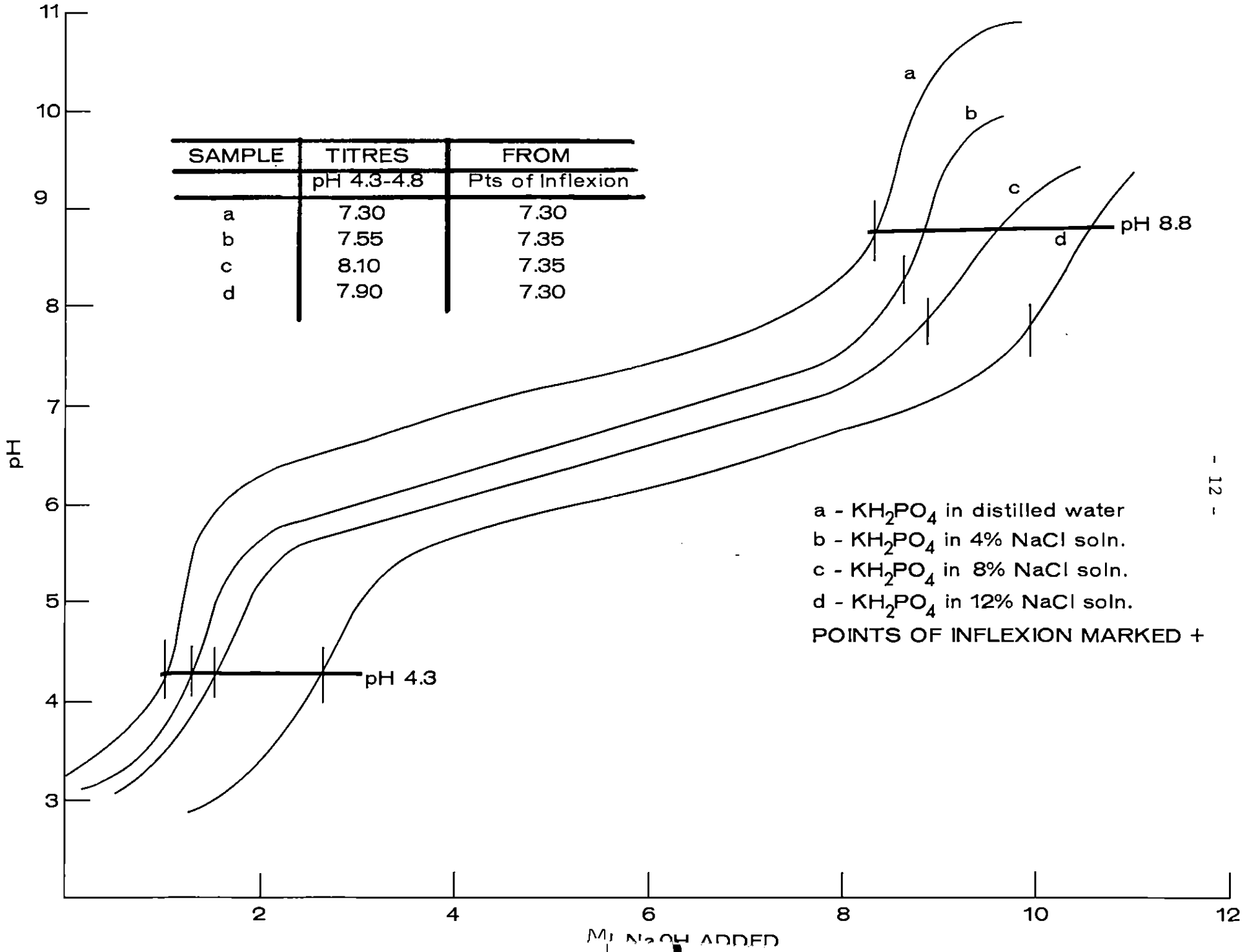
APPENDIX

TABLE I

RESULTS OF ANALYSES BY VARIOUS PROCEDURES

Detergent	Mod. Titrimetric Procedure (%P_2O_5)		Aut. Color. on Titration Solution (%P_2O_5)		ASTM Procedure as written (%P_2O_5)	
	Results	Mean	Results	Mean	Results	Mean
A	3.48		3.14, 3.18		3.71	
	3.26		3.20, 3.20		3.56	
	3.22		3.10, 3.18		3.68	
	3.3o	3.33	3.14, 3.14	3.16	3.87	3.71
B	4.51		4.60, 4.56		5.10	
	4.40		4.50, 4.50		4.94	
	4.61		4.54, 4.58		5.23	
	4.57	4.52	4.54, 4.46	4.53	4.82	5.04
C	4.73		4.58, 4.62		4.74	
	4.51		4.42, 4.46		5.32	
	4.62		4.50, 4.50		5.22	
	4.50	4.59	4.46, 4.54	4.51	5.04	5.08
D	3.56		3.60, 3.60		4.21	
	3.64		3.54, 3.66		4.42	
	3.80		3.58, 3.62		3.74	
	3.80	3.70	3.62, 3.66	3.61	4.61	4.25
E	4.34		4.40, 4.40		5.12	
	4.48		4.40, 4.40		4.86	
	4.38		4.34, 4.34		5.28	
	4.36	4.39	4.44, 4.46	4.40	5.63	5.22
F	3.92		3.88, 3.76		4.11	
	4.15		3.96, 3.86		4.61	
	3.95		3.92, 3.86		4.39	
	4.05	4.02	4.00, 3.96	3.90	4.43	4.39
G	3.59		3.54, 3.40		3.95	
	3.82		3.70, 3.60		4.19	
	3.72		3.50, 3.40		4.06	
	3.67	3.70	3.74, 3.60	3.56	3.96	4.04
H	4.68		4.44, 4.44		5.08	
	4.75		4.70, 4.60		5.44	
	4.70		4.58, 4.52		5.23	
	4.70	4.71	4.44, 4.44	4.52	5.36	5.28
I	4.44		4.25, 4.20		5.05	
	4.53		4.40, 4.44		4.87	
	4.61		4.40, 4.44		5.10	
	4.54	4.53	4.25, 4.20	4.32	5.10	5.03
Mean		4.16		4.06		4.67

FIGURE 1



SAMPLE	TITRES pH 4.3-4.8	FROM Pts of Inflexion
a	7.30	7.30
b	7.55	7.35
c	8.10	7.35
d	7.90	7.30

FIGURE 2

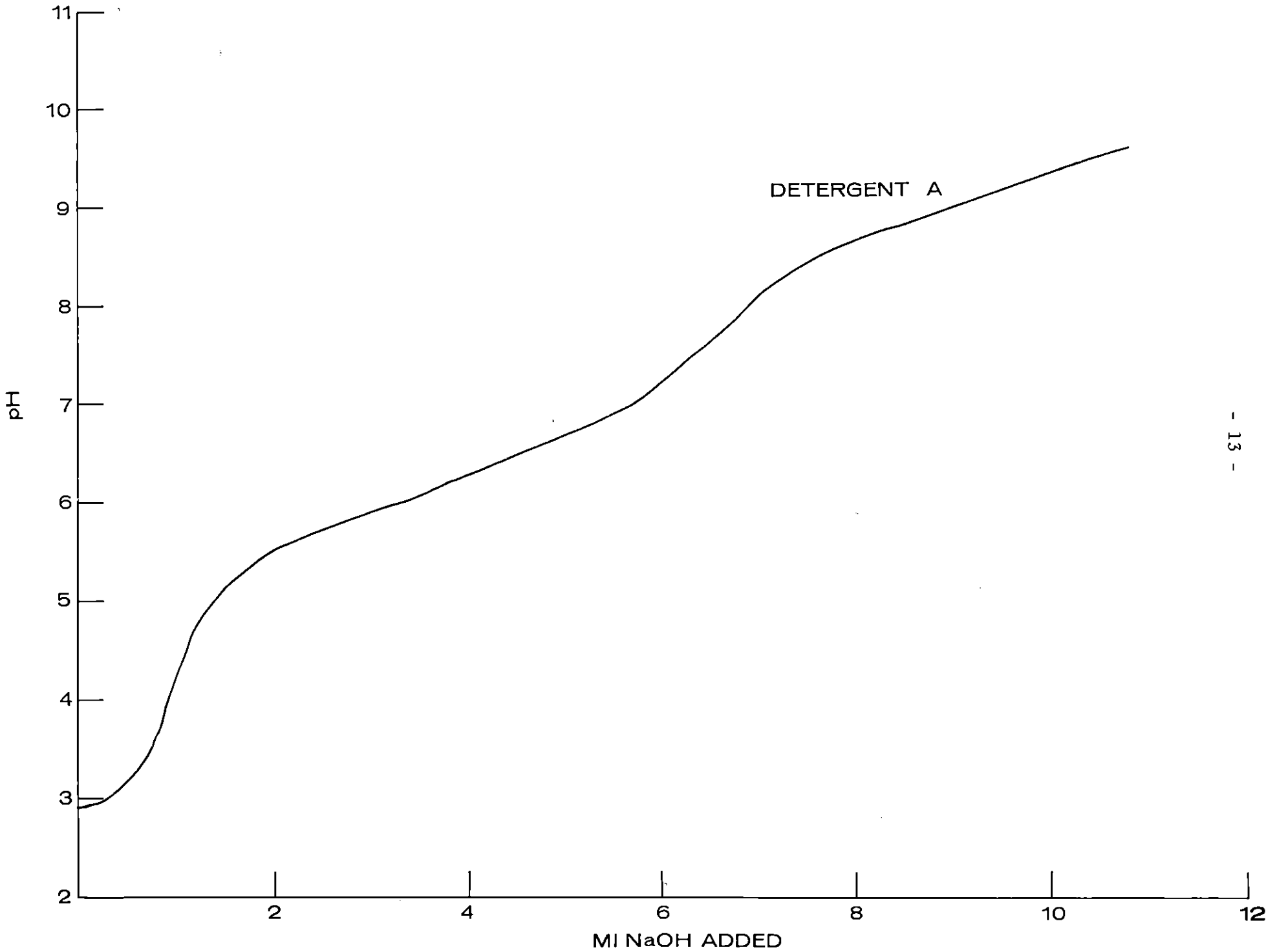


FIGURE 3

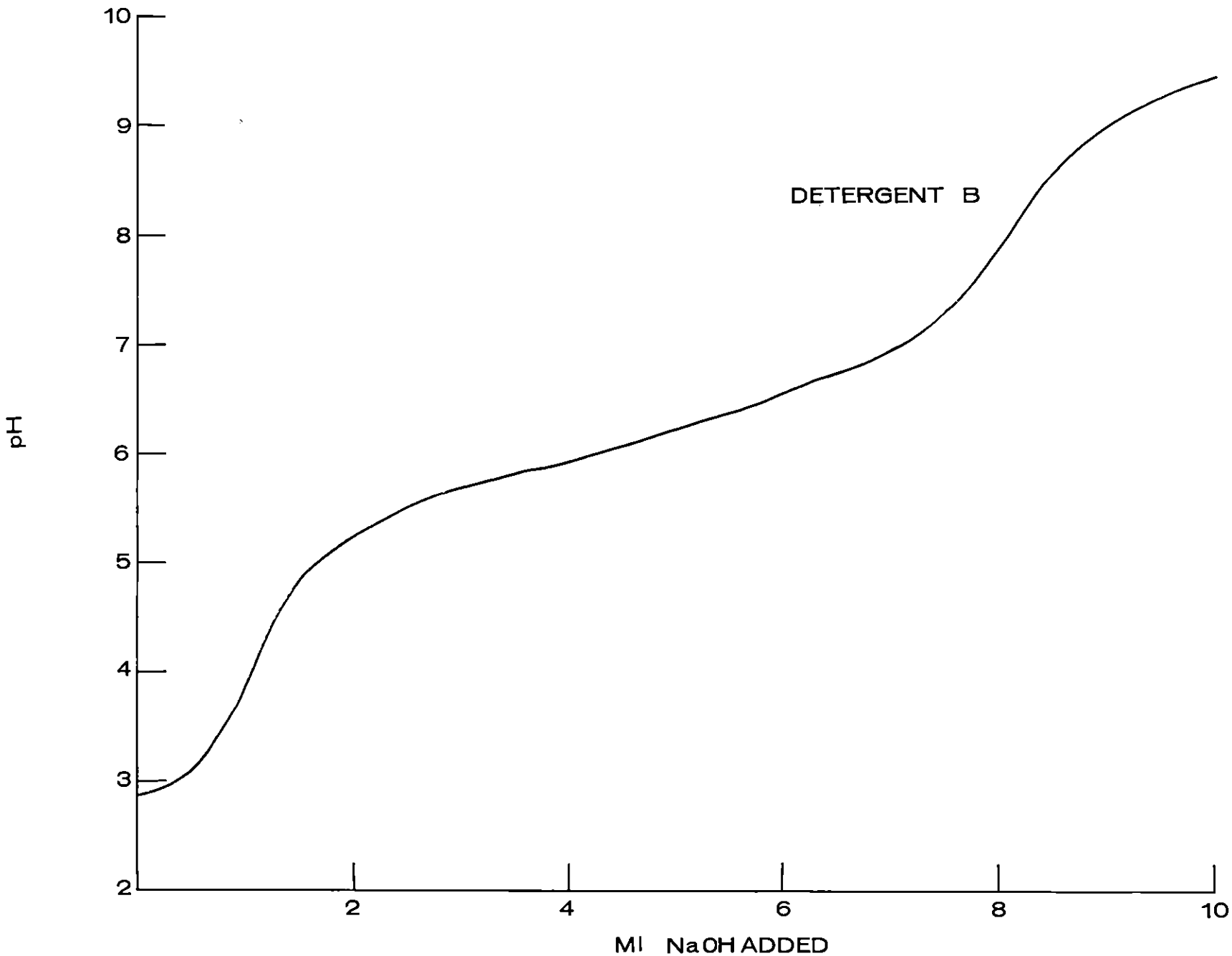


FIGURE 4

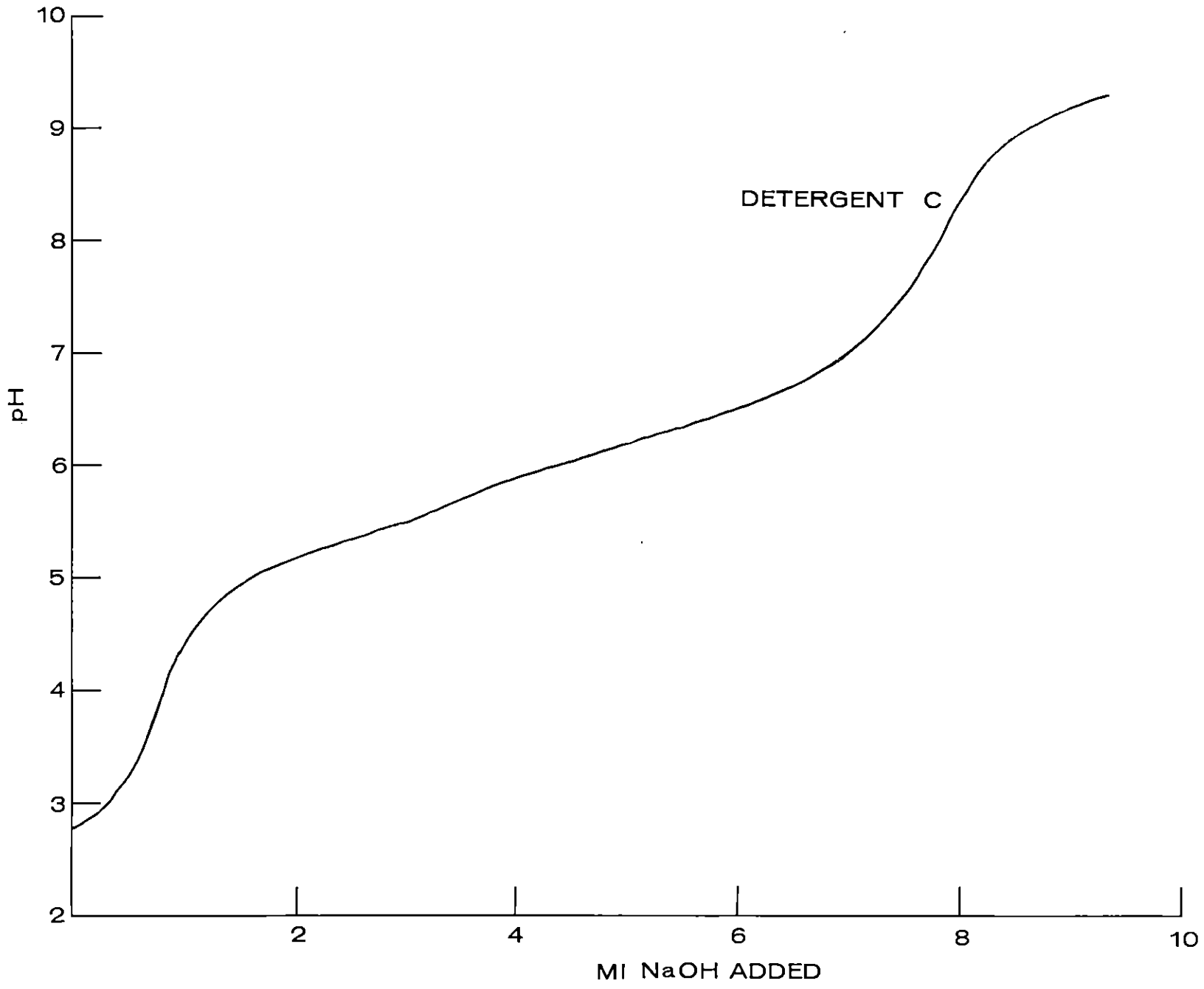


FIGURE 5

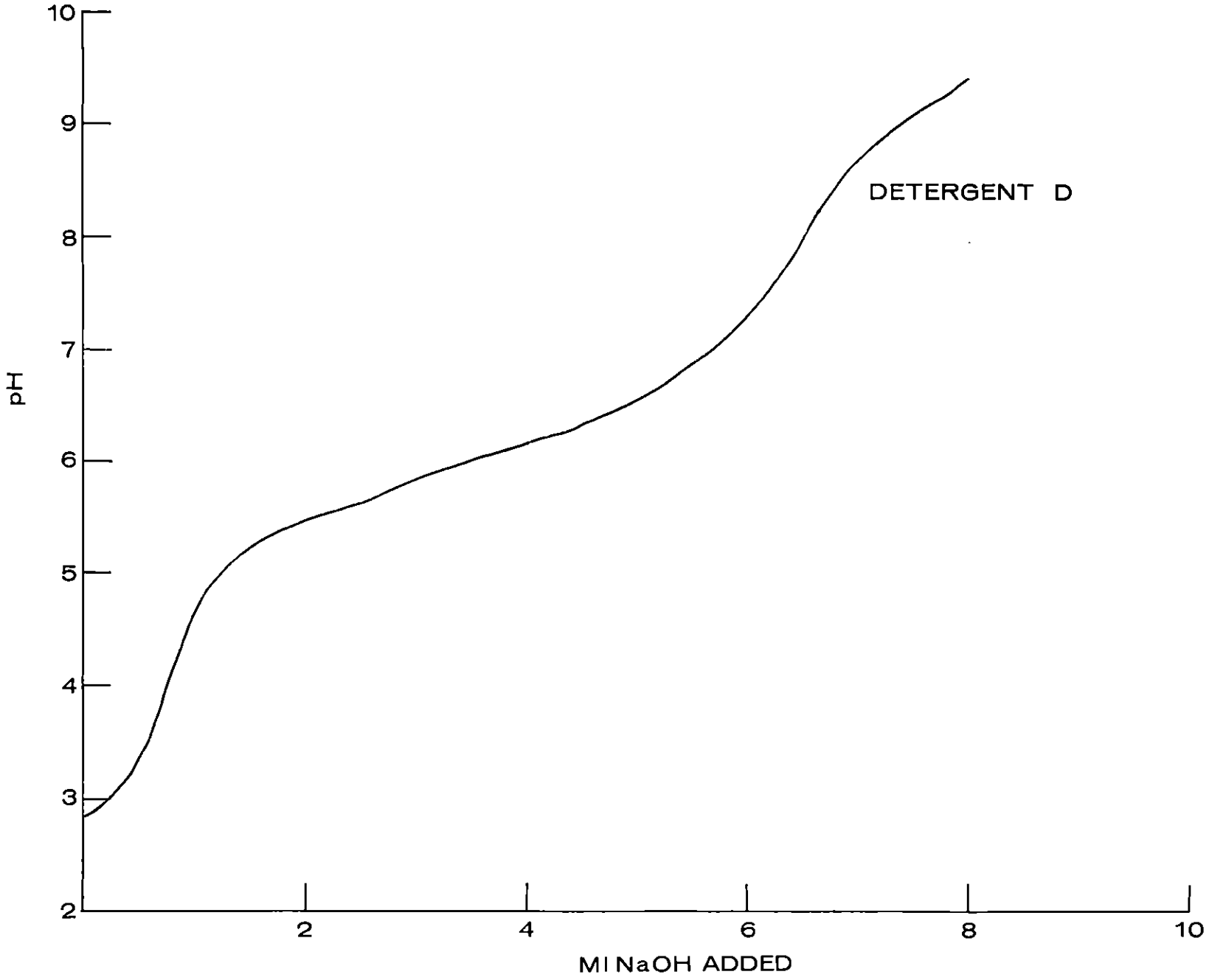


FIGURE 6

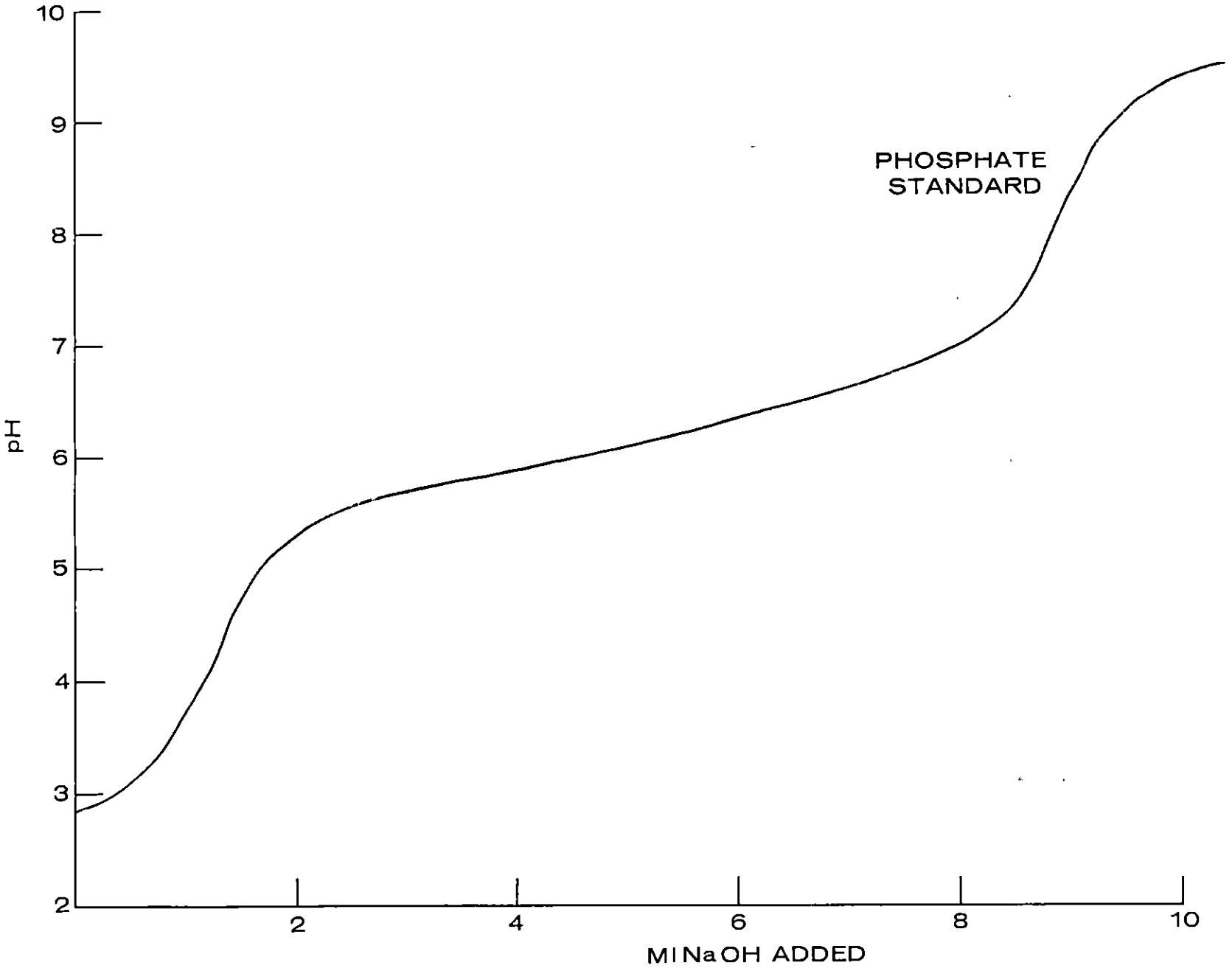


FIGURE 7

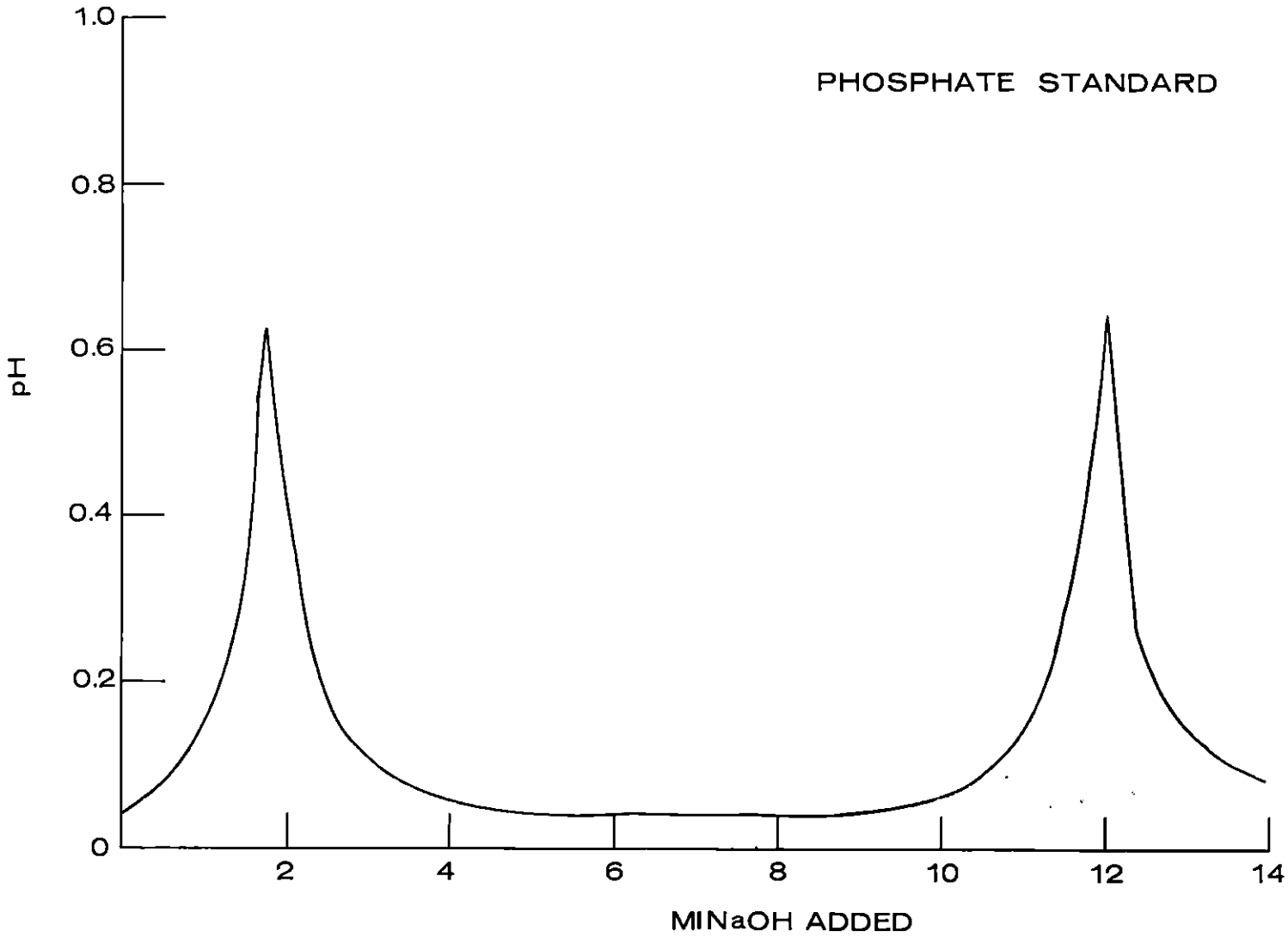

PHOSPHATE STANDARD
pH
1.0
0.8
0.6
0.4
0.2
0
2
4
6
8
10
12
14
MINaOH ADDED

FIGURE 8

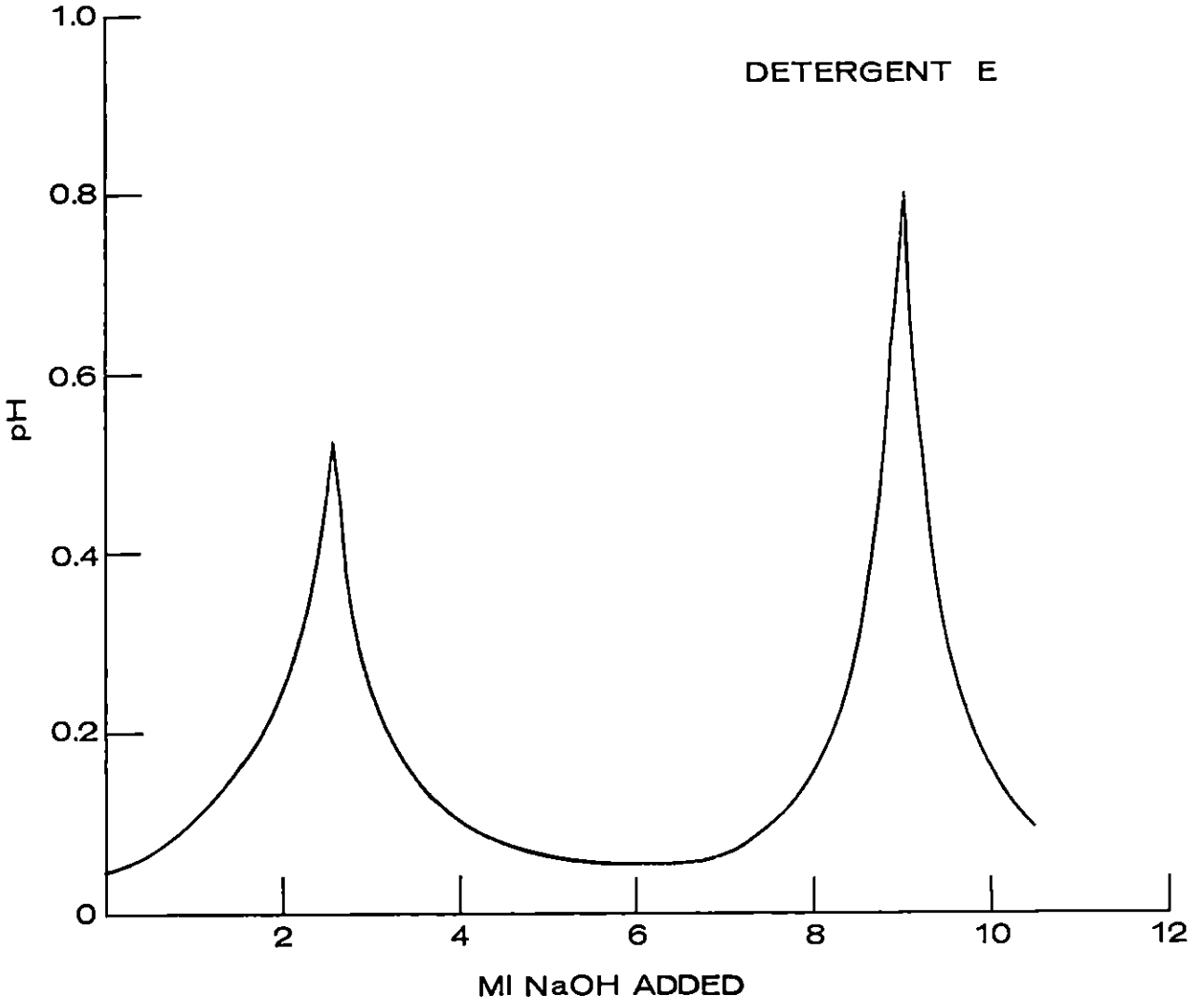
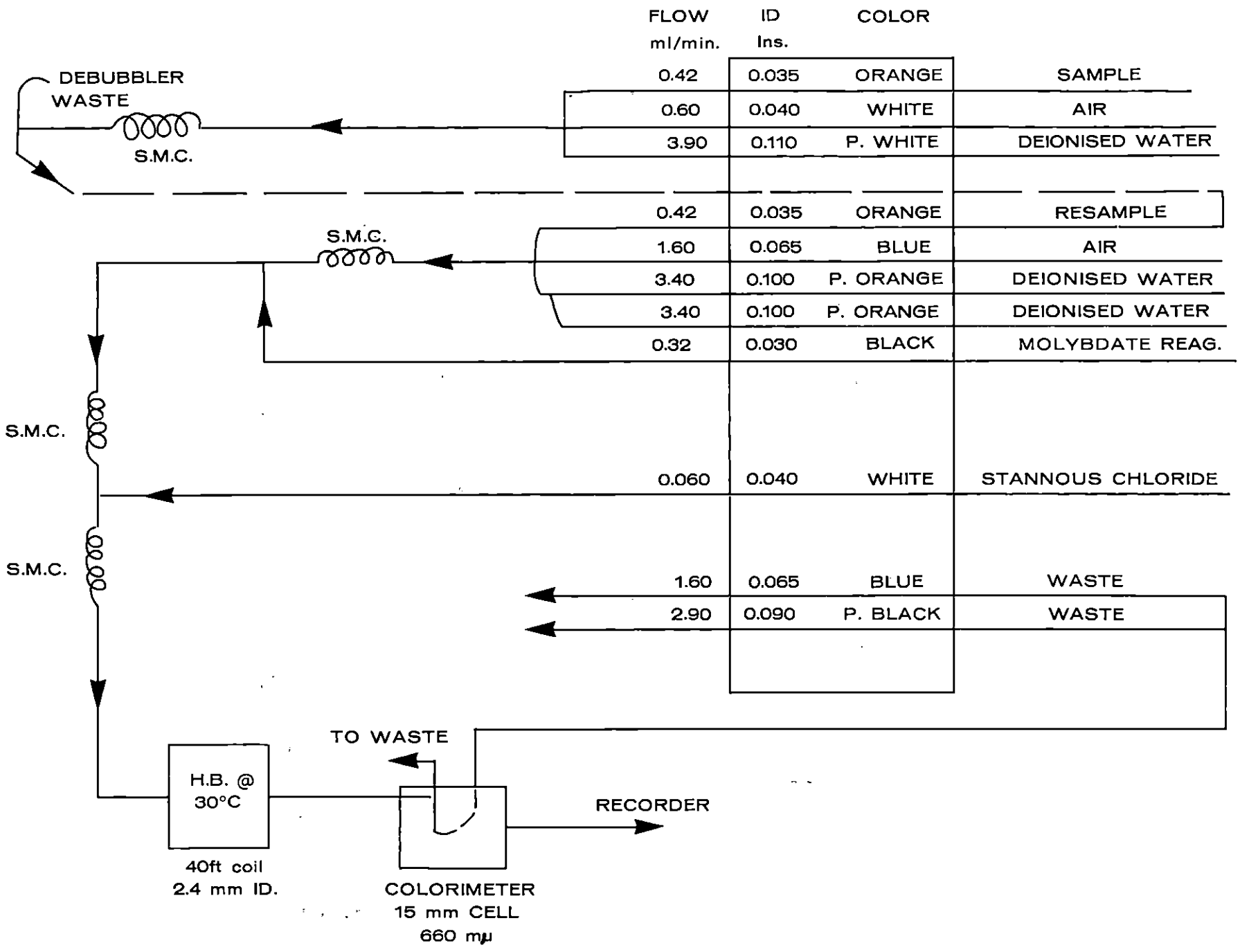


FIGURE 9


FLOW ml/min.
ID Ins.
COLOR
DEBUBBLER WASTE
S.M.C.
0.42 0.035 ORANGE SAMPLE
0.60 0.040 WHITE AIR
3.90 0.110 P. WHITE DEIONISED WATER
0.42 0.035 ORANGE RESAMPLE
S.M.C.
1.60 0.065 BLUE AIR
3.40 0.100 P. ORANGE DEIONISED WATER
3.40 0.100 P. ORANGE DEIONISED WATER
0.32 0.030 BLACK MOLYBDATE REAG.
S.M.C.
0.060 0.040 WHITE STANNOUS CHLORIDE
S.M.C.
1.60 0.065 BLUE WASTE
2.90 0.090 P. BLACK WASTE
TO WASTE
H.B. @ 30°C
RECORDER
40ft coil 2.4 mm ID.
COLORIMETER 15 mm CELL 660 mμ