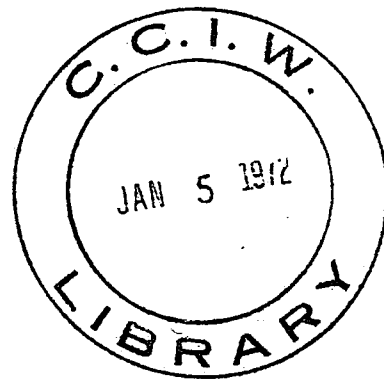


45



*Direct*  
**INLAND WATERS BRANCH**

**DEPARTMENT OF THE ENVIRONMENT**



# *The Determination of the Phosphorus Content of Detergents*

*P.D. GOULDEN, W.J. TRAVERSY and M. COMBA*

TECHNICAL BULLETIN NO.45

GB  
707  
C338  
no. 45



TECHNICAL BULLETIN NO.45

*The Determination of the Phosphorus Content of Detergents*

*P.D. GOULDEN, W.J. TRAVERSY and M. COMBA*

INLAND WATERS BRANCH  
DEPARTMENT OF THE ENVIRONMENT  
OTTAWA, CANADA, 1971

# Contents

	Page
SUMMARY . . . . .	v
INTRODUCTION . . . . .	1
PART I. Determining the Phosphorus Content of Detergents by a "Modified ASTM" Procedure. . . . .	1
1. Scope and Application. . . . .	1
2. Principle of the Method. . . . .	2
3. Interferences. . . . .	2
4. Sampling Procedure and Storage . . . . .	2
5. Sample Preparation . . . . .	2
6. Apparatus. . . . .	2
7. Reagents . . . . .	3
8. Procedure. . . . .	3
9. Calculations . . . . .	4
10. Precision and Accuracy . . . . .	4
PART II. Determining the Phosphorus Content of Detergents by an Automated Method . . . . .	4
1. Scope and Application. . . . .	4
2. Principle of the Method. . . . .	4
3. Interferences. . . . .	4
4. Sampling Procedure and Storage . . . . .	5
5. Sample Preparation . . . . .	5
6. Apparatus. . . . .	5
7. Reagents . . . . .	5
8. Procedure. . . . .	7
9. Calculations . . . . .	7
10. Precision and Accuracy . . . . .	8
REFERENCES . . . . .	8
APPENDIX . . . . .	9

## *Summary*

This publication describes the procedures used in the Water Quality Division laboratories to determine the phosphorus concentration of detergents. A manual method published by the American Society for Testing and Materials (ASTM), modified to overcome the interference from borates, is used to analyze samples that have a phosphorus concentration close to the 20%  $P_2O_5$  maximum specified in the Phosphorus Concentration Control Regulations. An automated method has been developed, using "Technicon AutoAnalyzer" equipment, that enables detergent samples to be screened for phosphorus content at a rate of 20 samples per hour.

# *The Determination of the Phosphorus Content of Detergents*

**P.D. GOULDEN, W.J. TRAVERSY and M. COMBA**

## INTRODUCTION

The regulations respecting the control of phosphorus concentration in cleaning agents (shown in Appendix) have restricted the amount of phosphorus in any laundry detergent manufactured in Canada, or imported into Canada, after August 1st, 1970. Under the regulations, the maximum permissible amount of phosphorus in these products is 20% by weight expressed as phosphorus pentoxide ( $P_2O_5$ ). The Water Quality Division of the Inland Waters Branch is carrying out the analyses of the detergent samples in the program of enforcement of the regulations.

The regulations specify that the method of analysis shall be the method prescribed by ASTM. However, while recognizing that certain materials present in some detergents may interfere with the method, the ASTM publication does not give procedures for overcoming this interference. In particular, the presence of borates, which may be added as borax or sodium perborate in detergent manufacture, leads to an erroneously high phosphorus result in the method. In Part I below is given the procedure followed in the Water Quality Division laboratory to determine the phosphorus content of detergents using the ASTM procedure modified to remove this interference from borates.

The "Modified ASTM" method is a manual procedure which is quite time consuming. Many of the samples analyzed have phosphorus concentrations much below the 20%  $P_2O_5$  limit and it is desirable to use an automated method for analysis that will provide a screening so that only those detergents close to the limit need be analyzed by the "Modified ASTM" method. The automated procedure which is described below has been developed and enables detergents to be analyzed for phosphorus in "Technicon AutoAnalyzer" equipment at a rate of 20 samples per hour.

## PART I. DETERMINING THE PHOSPHORUS CONTENT OF DETERGENTS BY A "MODIFIED ASTM" PROCEDURE

### 1. Scope and Application

The method is applicable to any laundry detergent. The method defines levels of phosphorus down to 0.5%  $P_2O_5$  but can be used for all higher concentrations.

## 2. Principle of the Method

The method consists of converting all of the phosphate in a sample to orthophosphate by acid hydrolysis and titrating with sodium hydroxide between the two end points of orthophosphoric acid. Each sample is charred over a burner and ignited at 550°C to destroy organic material that might interfere with the test.

## 3. Interferences

The titration is one of sodium hydroxide against the weak acids that are present in the treated sample. The method is a valid one because the procedure removes weak acids other than orthophosphate, such as carbonate, organic acids and borates.

As a check on the freedom from interference, the following materials were investigated.

Borates - Five samples of one detergent were enriched with known amounts of sodium perborate. No interference was noted up to 20% sodium perborate in the sample.

Silica - Five samples of one detergent were enriched with sodium metasilicate to concentrations varying from 10% to 90% and analysed for phosphate concentration. No interference was noted and the mean recovery was 99.9% for the five samples.

NTA - As nitrilotriacetic acid is being added to some detergents the possibility of interference from this chemical was investigated. Five samples of one detergent were enriched with NTA to concentrations varying from 10% to 50% and analysed for phosphate. No interference was observed and the mean recovery was 99.6%  $P_2O_5$ .

## 4. Sampling Procedure and Storage

The sample normally is represented by an unopened carton of laundry detergent. This carton is stored in a polyethylene bag, tied to prevent loss of moisture or other volatile material from the carton. If the sample is in an opened carton or similar sample container, it is transferred for storage to a bottle with a screw cap.

## 5. Sample Preparation

The carton is cut open and the detergent riffled until it is approximately 250 ml in volume. This 250 ml is then ground in a "Waring" blender at high speed for two minutes. Portions of this ground product are then used for the determination; the remainder is stored in a sealed container against the need for repeat analysis.

## 6. Apparatus

- 6.1. Set of riffles, e.g., Jones samplers.
- 6.2. "Waring" blender or equivalent.

- 6.3. pH meter.
- 6.4. Muffle furnace.
- 6.5. Porcelain casseroles, 150-ml capacity.

#### 7. Reagents

- 7.1. Hydrochloric acid - reagent grade.
- 7.2. Methyl alcohol - reagent grade.
- 7.3. NaOH solution - 30% solution of reagent grade material - prepared so as to be free of carbonate.
- 7.4. NaOH solution - 0.5N.

#### 8. Procedure

- 8.1. Weigh a representative sample of 2.5 g.
- 8.2. Place in a porcelain evaporating dish and char gently over a gas burner to expel volatile matter.
- 8.3. Transfer the dish with its contents to a muffle furnace operated at 550°C for 30 min. The ignited residue need not be free of carbon.
- 8.4. Allow the sample to cool and cautiously add 10 ml concentrated HCl. Cover the sample with a ribbed pyrex watch glass and evaporate to dryness. Avoid splattering.
- 8.5. Treat the residue with 10-ml portions of a methyl alcohol-acid solution (10 parts methanol + 1 part concentrated HCl) and evaporate gently on a hot plate. Ignite the vapour. If borates are present, the flame will be a green colour. Continue the additions of alcohol acid solution until the flame is a normal yellow colour.
- 8.6. Evaporate to dryness, take up with 50 ml of water and 10 ml HCl, and transfer quantitatively to a 400-ml beaker. Make up the volume to about 300 ml with distilled water. Cover with a watch glass and boil gently for 60 minutes. Cool.
- 8.7. If necessary, dilute the sample to 200 ml and titrate to a pH of 3.0 with 30% NaOH solution. Cool again and adjust the pH to 4.3 with the standard NaOH solution.
- 8.8. Titrate carefully with the standard NaOH solution (Ca 0.5N) from pH 4.3 to the upper end point (pH 8.8) recording the volume of NaOH required (T).

## 9. Calculations

Calculate the percentage  $P_2O_5$  as follows:

$$\text{Total } P_2O_5 \text{ per cent} = \frac{TN \times 7.098}{W}$$

where: T = milliliters of NaOH solution required for titration of the sample.

N = normality of NaOH solution.

W = grams of sample in the sample solution.

## 10. Precision and Accuracy

- 10.1. Determination of the phosphorus content of a single detergent gave a coefficient of variation of 1.3% at a  $P_2O_5$  level of 20% calculated for ten replicates.
- 10.2. Standard additions of sodium tripolyphosphate to ten detergent samples gave a mean recovery of 99.8% of the theoretical amount.
- 10.3. Analysis of the standard  $KH_2PO_4$  treated as a detergent sample gave, for ten replicates, a mean value of 52.5%  $P_2O_5$ , with a coefficient of variation of 0.9% (Theoretical value for  $KH_2PO_4$  is 52.2%  $P_2O_5$ ).

## PART II. DETERMINING THE PHOSPHORUS CONTENT OF DETERGENTS BY AN AUTOMATED METHOD

### 1. Scope and Application

The method is applicable to any laundry detergent. Phosphorus levels from 0.5 to 50%  $P_2O_5$  can be measured by choice of appropriate standards. In the particular application of this method in the Water Quality laboratory, phosphorus levels in the range from 14 to 23%  $P_2O_5$  are determined.

### 2. Principle of the Method

In this method the detergent is dissolved in water and heated with potassium persulfate and sulfuric acid to destroy a large part of the organic material and to hydrolyze the polyphosphates to orthophosphates. The solution is then diluted in a "Technicon AutoAnalyzer" system, ammonium molybdate is added to form the heteropolymolybdophosphoric acid, and this complex is then reduced to molybdenum blue with stannous chloride. Because of the great dilution in the system and the high sensitivity of the stannous chloride - molybdenum blue determination, it is possible to run the digested detergent solution directly without filtration or dialysis.

### 3. Interferences

The method has been tested for interference from materials commonly found in detergents, namely, silicate, synthetic surfactant, soap, NTA, sodium citrate, carbonate, optical brightener, sodium perborate and borax. No interference with the method was found from any of these materials at any concentration that is probable in a laundry detergent formulation.



#### 4. Sampling Procedure and Storage

The sample normally is represented by an unopened carton of laundry detergent. This carton is stored in a polyethylene bag, tied to prevent loss of moisture or other volatile material from the carton. If the sample is in an opened carton or similar sample container, it is transferred for storage to a bottle with a screw cap.

#### 5. Sample Preparation

The carton is cut open and the detergent riffled until it is approximately 250 ml in volume. This 250 ml is then ground in a Waring blender at high speed for two minutes. Portions of this ground product are then used for the determination; the remainder is stored in a sealed container against the need for repeat analysis.

#### 6. Apparatus

- 6.1. Set of riffles, e.g., Jones samplers.
- 6.2. "Waring" blender.
- 6.3. "FISHER" oscillating hot plate, or equivalent.
- 6.4. A "Technicon AutoAnalyzer" unit consisting of:

Sampler II,  
Manifold - (see Figure I),  
Two proportioning pumps or one pump II,  
Colorimeter containing a 15-mm flow cell and a 660-mu filter.

- 6.5. A water/steam bath at 100°C.
- 6.6. 100-ml volumetric flasks.
- 6.7. "FISHER" volustat or equivalent.

#### 7. Reagents

- 7.1. Ammonium molybdate solution: dissolve 25 g  $(\text{NH}_4)_6\text{MO}_7\text{O}_{24}4\text{H}_2\text{O}$  in 175 ml distilled water. To 400 ml distilled water add 280 ml conc  $\text{H}_2\text{SO}_4$ . Add the molybdate solution to the acid solution and dilute to 1 litre.
- 7.2. Stannous chloride solution (1) Stock: dissolve 5 g  $\text{SnCl}_2\cdot 2\text{H}_2\text{O}$  in 25 ml conc  $\text{HCl}$  and dilute to 500 ml with distilled water; this stock is stable for 2 weeks at 5°C storage. (2) Working solution: to 30 ml stock add 25 ml conc  $\text{HCl}$  and dilute to 500 ml with distilled water; this batch is stable for 12 hours.
- 7.3. Strong acid solution: to 600 ml distilled water add 300 ml conc  $\text{H}_2\text{SO}_4$ ; cool and add 4 ml  $\text{HNO}_3$ ; cool and dilute to 1 litre.

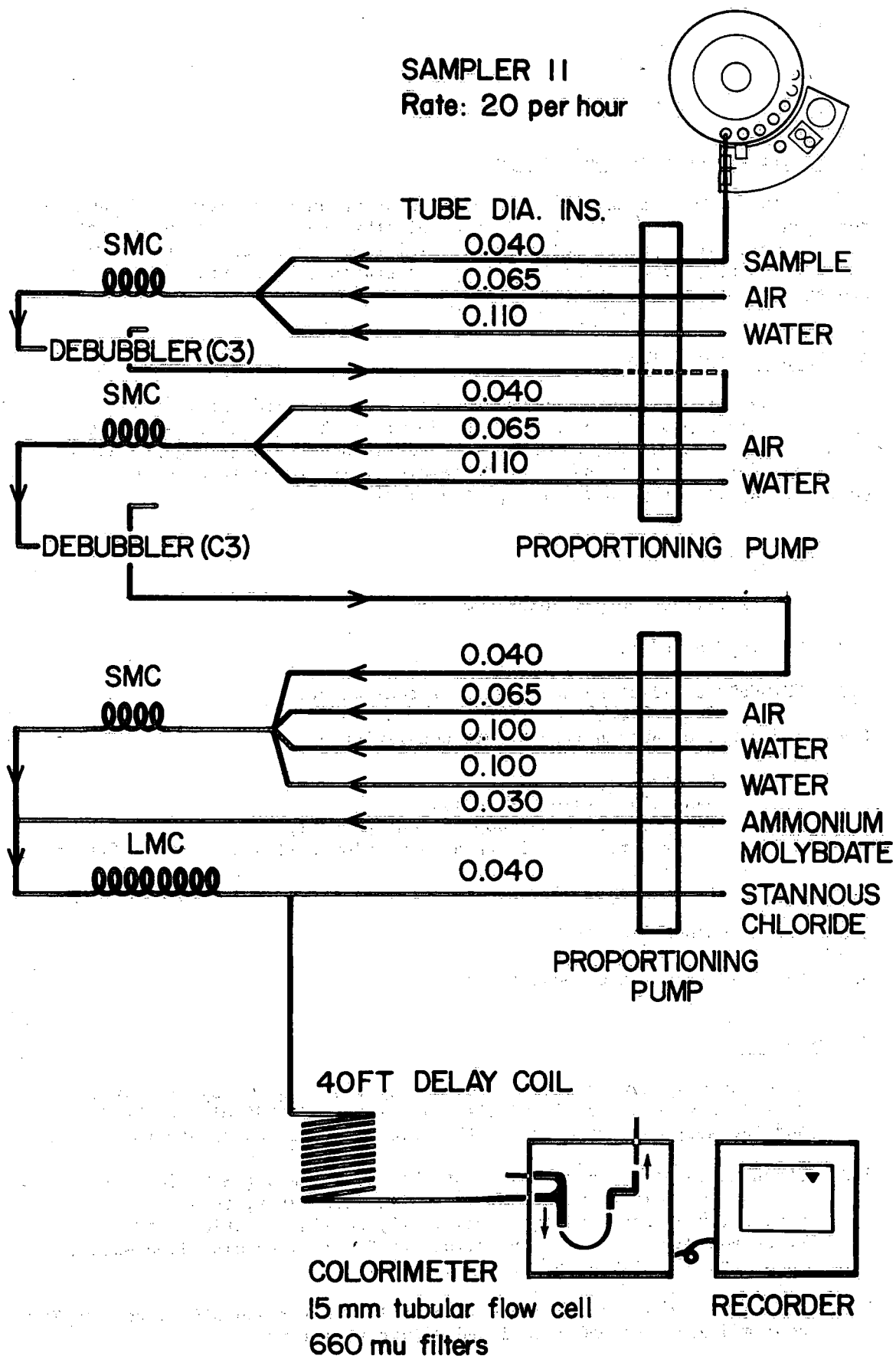


Figure 1. Manifold for automated phosphorus determination.

- 7.4. Potassium persulfate: solid form ACS grade.
- 7.5. Potassium dihydrogen phosphate: reagent grade, oven-dried at 105°C.
- 7.6. Sodium tripolyphosphate: granular - purified.

## 8. Procedure

- 8.1. Weigh approximately 1.0 g of detergent into a dry 100-ml volumetric flask.
- 8.2. Add approximately 40 ml water.
- 8.3. Place flask on oscillating hot plate for about 30 minutes. The heat setting of the hot plate is adjusted so that the temperature of the solution is 60-70°C after 30 minutes. (The 14½ inch by 18½ inch hot plate used accommodates 40 flasks).
- 8.4. Allow the flask to cool.
- 8.5. Add 10 ml strong acid from the volustat and about 4 g potassium persulfate (the potassium persulfate is measured with a scoop).  
N.B. If the detergent should contain a large amount of carbonate, there will be a violent evolution of CO<sub>2</sub> when acid is added. Hence, when analyzing unknown detergents or detergents known to contain carbonate, the acid should be added drop by drop initially.
- 8.6. Heat the flask in the steam/water bath at 100°C for one hour.
- 8.7. Allow the flask to cool to room temperature and make up to 100 ml volume.
- 8.8. With the manifold as shown in Figure I, run the samples through the "AutoAnalyzer" system.
- 8.9. Make up standards by weighing 0.4 g, 0.35 g, 0.30 g and 0.25 g of sodium tripolyphosphate and treating these as above. Periodically (every two weeks) compare the peak heights obtained from tripolyphosphate standard solutions with those obtained from potassium dihydrogen phosphate standards in order to calibrate the phosphorus content of the sodium tripolyphosphate used. (Since STPP is hydroscopic, it should be kept in a tightly sealed container.)

## 9. Calculations

- 9.1. Prepare a calibration curve from peak heights obtained with the STPP standards, calibrated from the periodic check against the potassium dihydrogen phosphate.
- 9.2. From the calibration curve, the peak heights, and the amount of detergent weighed out, determine the phosphorus content of the detergents.

10. Precision and Accuracy

- 10.1. Determining the phosphorus content of a single detergent gave a coefficient of variation of 2.3% at a  $P_2O_5$  level of 18%, calculated for ten replicates.
- 10.2. Paired determinations of phosphorus levels for forty detergent samples tested by the automated method and the "Modified ASTM" method showed no significant difference for the two methods.

REFERENCES

American Society for Testing and Materials, 1969. Part 22, Method D820.

## APPENDIX

### REGULATIONS RESPECTING THE CONTROL OF PHOSPHORUS CONCENTRATION IN CLEANING AGENTS

1. These Regulations may be cited as the Phosphorus Concentration Control Regulations.

#### Prescribed Nutrients

2. Phosphorus and all compounds thereof are prescribed as nutrients for the purpose of section 18 of the Canada Water Act.

#### Laundry Detergents

3. On and after the 1st day of August, 1970, the maximum permissible concentration of prescribed nutrients in laundry detergents shall be 20 per cent by weight expressed as phosphorus pentoxide or 8.7 per cent by weight expressed as elemental phosphorus.
4. The concentration by weight of prescribed nutrients in any laundry detergent shall be determined by the method prescribed from time to time by the American Society for Testing and Materials, (ASTM).

Environment Canada Library, Burlington



3 9055 1017 3385 4

