The use of oxidation reactor for water sample preparation in the total phosphate determination using Segmented Flow Analysis

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Abstract. The pollution in surface waters such as rivers, lakes/reservoirs and estuarine is mostly caused by domestic waste; one of them is detergent. Detergents used in households contain phosphate that disrupts the ecosystem. In the determination of detergents, sample preparation is one of the most important stages. This study describes the use of an oxidation reactor with UV radiation for the destruction of total phosphate compounds in detergent into dissolved phosphates in the preparation stage of detergent determination. With this method, the destruction of total phosphate in detergent samples required a very short time and could be connected directly to the Segmented Flow Analysis device. In this study, the oxidation reactor was tested on artificial samples containing 0.5% detergent and water samples from the Citarum and Cikapundung Rivers (Bandung, Indonesia) which were estimated to be contaminated with detergent. The average concentrations of total phosphate of the samples from Cikapundung and Citarum were 4.5773 ± 0.2286 mg-PO₄³⁻/l and 4.1841 ± 0.0361 mg-PO₄³⁻/l, respectively. Meanwhile, the average concentration of total phosphate of the artificial sample was 5.5727 ± 0.1830 mg-PO₄³⁻/l. The results show that the sample digestion method using UV radiation in the oxidation reactor can provide excellent results with a high recovery at 94.51%.

1. Introduction
In developing countries, environmental pollution issues have been arising significantly as a result of industrialization and population growth. The pollutions are high enough to cause environmental problems due to the unprocessed waste disposal including industrial waste and domestic waste [1]. One of the wastes that flow into rivers, reservoirs, lakes and seas is phosphate compounds, both in the form of orthophosphate and polyphosphate compounds [2]. Phosphate compounds that flow into public stream come from many sources such as runoff, land erosion, animal waste, composting and urban waste. In the watershed, the contribution of phosphate varies based on land use, for example, the main sources of organic compound in slum or village area are from human feces. Human feces pollute the public stream at a load of approximately 0.7 kg/person/year, while pollution from detergent is approximately 0.75-1 kg-PO₄³⁻/people/year. It is estimated that around 50-75% of the phosphate compounds present in lakes, reservoirs, and rivers are originated of detergent waste [3]. Phosphate in the form of sodium tripolyphosphates (STTP, Na₅P₃O₁₀) is the most commonly used builder in the detergent, which forms complexes with Ca²⁺ and Mg²⁺ ions, creating a favorable condition for detergent action by reducing the hardness of water. Soda ash, sodium chloride, sodium sulphate, sodium silicate and zeolite are also used as builders in the detergent, however, STPP is preferred largely due to its greater ability to clean [4].
The phosphate itself has no toxicity. It is one of the important nutrients needed by living organisms, but in a large quantity, phosphate would be excessive and cause eutrophication in the water, which bring to the consequence of oxygen depletion in water. It happens because of the excessive growth of algae (phytoplankton). Algae biomass that has died and deposited at the bottom of the water body is a source of organic food for various types of microorganisms such as bacteria. The availability of many food sources can increase the growth rate of bacteria. The excessive bacterial population will consume dissolved oxygen in the water so that it can endanger the life of the surrounding water organisms [5].

A recent report of the United Nation Environmental Programme (UNEP) indicates that globally around 30-40% of the lakes and reservoirs have been affected by eutrophication. Eutrophication is the natural ageing of streams or lakes by nutrient enrichment or algae and phytoplankton, causing several problems such as lack of oxygen needed for fish and higher mortality rate; thus, disrupting the normal functioning of the aquatic ecosystem [4]. Therefore it is very important to precisely determine the phosphate content in the water samples.

There are several sample preparation methods commonly used for destruction of total phosphate from detergent contaminated water samples into dissolved phosphate, including destruction by perchloric acid, nitrate-sulfuric acid and persulfate. The weakness of these methods is they require a long time, prone to explosion when the heating is out of control, and the exhaust is very corrosive acid vapor. For this reason, a more environmentally friendly method should be developed both for the off-line and on-line monitoring system. Development of sample preparation method for determination of total phosphate from surface water samples has to improve the current analytical methods such as shorter analysis time, lower use of chemicals and high accuracy [5].

Segmented Flow Analysis techniques are established devices for automated analysis, which provide benefits such as: (i) increased injection throughput, (ii) high versatility, (iii) high durability, (iv) new analytical enhancements based on operating modes in non-stationary conditions, (v) decreasing human exposure under hazardous chemical/physical sample pretreatment, and (vi) procedures that are more environmentally friendly for using less chemicals. In this study, a continuous flow sample preparation method was developed and used, in which water samples containing phosphate were mixed with a solution of persulfate in an acidic condition through heating at 60 °C and a UV radiation source (325 nm). The total phosphate was determined with a segmented flow analysis equipment at the wavelength of 660 nm [6].

2. Methodology

2.1. Chemicals and instruments

The chemicals used for this study were sulfuric acid (H$_2$SO$_4$), ascorbic acid (C$_6$H$_8$O$_6$), detergent, potassium dihydrogen phosphate (KH$_2$PO$_4$), potassium peroxodisulfate (K$_2$S$_2$O$_8$) and ammonium molybdate ((NH$_4$)$_6$Mo$_7$O$_{24}$.4H$_2$O). All chemicals used were of analytical grade from E-Merk. Demineralized water was generated from a demineralizer apparatus. The measurements were performed using a Segmented Flow Analysis (SFA-Perstorp) equipped with a pH-meter (E52 Metrohm), a recorder (Cole-Palmer), an oxidation reactor (OR-01 model, self-production). A vertical water sampler was used for sample collection.

2.2. Sample and solution preparation

In this study, artificial sample (0.5% w/v detergent solution) and surface water samples were used. Surface water samples were taken from the Cikapundung River and Citarum River (Bandung, Indonesia).

The solutions used in this study were 100 ppm standard solution, 50 ppm standard solution and mixed solution. The standard solution was made from potassium dihydrogen phosphate (KH$_2$PO$_4$). KH$_2$PO$_4$ crystal was dried in an oven at 105°C-110°C for 1 hour, then 0.439 g of dried KH$_2$PO$_4$ was dissolved in demineralized water and diluted to 100 ml. Mixed solution was made from 50 ml of sulfuric acid (5 N H$_2$SO$_4$) added with 15 ml of 4% ammonium molybdate ((NH$_4$)$_6$Mo$_7$O$_{24}$), 30 ml of ascorbic acid (0.1 N
C₆H₈O₆ and 5 ml of antimonyl tartrate potassium (0.007 N K₅SbOC₄H₆O₆), then set to room temperature [7]. If the solution precipitated, the solution was shaken until the sediment was re-dissolved. Potassium persulfate solution (K₂S₂O₈) was added to samples to be analyzed under acidic conditions, then the samples were flowed through the peristaltic pump to the heater (60°C) in the SFA equipment at a flow rate of 3 ml/minute. Then the heated solution was flowed to the oxidation reactor unit and held for the total oxidation of the samples, it should not pass through the oxidizing reactor. After total oxidation was reached, the samples were flowed into the reactor mixing unit to be mixed with ammonium molybdate to form a yellow phosphomolybdate solution, followed by reduction by ascorbic acid to a perfectly formed blue color known as blue molybdenum [8,9]. The complex solution was flowed by a peristaltic pump to a flowcell detector (660 nm), where the total phosphate concentration of each sample would be determined by measuring the height of the recording peak and plotted onto the phosphate calibration curve. The resulting peak height is proportional to the phosphate concentration in the water sample [10]. As a control, water samples were flowed directly to the mixing unit without passing through the oxidation reactor.

Reactions occurred can be expressed by the following equations:

\[
\text{Poly phosphate (0.5% detergent solution) + K}_2\text{S}_2\text{O}_8 + \text{hv} \rightarrow \text{ortho-phosphate (PO}_4^{3-})
\]

\[
\text{PO}_4^{3-} + 3\text{NH}_4^+ + 12\text{MoO}_4^{2-} + 24\text{H}^+ \rightarrow (\text{NH}_4)_3[\text{P(Mo}_3\text{O}_10\text{)}_4]\ + 12\text{H}_2\text{O}
\]  (1)

Potassium antimonyl tartrate functioned to complete the reduction of the blue molybdenum complex and also to increase the intensity of the blue color produced by the following reaction.

\[
(\text{NH}_4)_3[\text{P(Mo}_3\text{O}_10\text{)}_4] + \text{C}_6\text{H}_8\text{O}_6 + 4\text{H}_2\text{O} \rightarrow \text{H}_3\text{PO}_4[\text{Mo}_12\text{O}_{40}] + \text{C}_6\text{H}_6\text{O}_6 + 3\text{NH}_4^+ + 7\text{H}^+ + 10e
\]  (2)

3. Result and discussion

3.1. Operational conditions of Segmented Flow Analysis equipment for total phosphate analysis of water sample

Before performing the total phosphate analysis, the operational conditions of Segmented Flow Analysis were firstly determined to get the optimum condition for total phosphate concentration determination [11].

Figure 1. Segmented Flow Analysis scheme made by Perstorp with oxidation reactor

Note: The dashed line (---) means the flow of control sample without going through the oxidation reactor
Table 1. Measurement condition with Segmented Flow Analysis (SFA).

| Condition                | Unit | Measure |
|--------------------------|------|---------|
| Wavelength               | nm   | 660     |
| SFA peristaltic pump speed | %    | 40      |
| Sample time              | s    | 55      |
| Washing time             | s    | 75      |
| Rise time                | S    | 10      |
| Range                    | AUFS | 0.5     |

3.2. Determination of total phosphate concentration range used in the Segmented Flow Analysis equipment

The molybdenum blue method can be used to total phosphate analysis of water sample in the concentration range from 0.01 to 1.6 mg-P/l at the wavelength of 660 nm or 880 nm.

Figure 2. Useful Concentration Range (UCR) for total phosphate analysis.

Based on the results of standard phosphate solution determination using Segmented Flow Analysis (Figure 2), it can be seen that the curve of a standard phosphate solution (PO$_4^{3-}$) was a combination of two segmented linear ranges: 1 to 4 mg-PO$_4^{3-}$/l and 4 to 7 mg-PO$_4^{3-}$/l. Each concentration range had a correlation coefficient of $r > 0.995$, which means both ranges could be used in the determination of the total phosphate concentration by using the SFA equipment.

3.3. Repeatability test of Segmented Flow Analysis equipment

To find out the accuracy of the SFA for orthophosphate analysis, a repeatability test using standard solution (5 mg-PO$_4^{3-}$/l) was carried out with six times repeat. Figure 3 shows that the Segmented Flow Analysis equipment had good repeatability (R) because it provided a small peak value (height) deviation. The differences between measurements were not much.

To find out the total phosphate concentration in the sample, total phosphate calibration curve must be made by measuring the absorption value by each concentration of the standard phosphate solution with a concentration range of 1.0–4.0 mg-PO$_4^{3-}$/l (taken from UCR test in Figure 2). From this measurement, phosphate concentration ($y$) can be obtained using the linear equation: $y = 0.391 \times -0.0106$, with correlation coefficient value: $r > 0.995$. This value shows that the calibration curve has good linearity [10,12].
Figure 3. Repeatability curve of standard solution 5 mg-PO$_4^{3-}$/l.

Figure 4. Calibration curve of total phosphate (PO$_4^{3-}$).

3.4. Determination of artificial sample (0.5% detergent solution) without oxidation reactor

Table 2 shows that even though the artificial sample was mixed with 20% H$_2$SO$_4$ and 2.6% K$_2$S$_2$O$_8$ as well as heated at 60°C, without UV radiation, only a small portion of organic phosphate in the artificial sample (0.5% detergent) had been destructed, which was 0.43 mg-PO$_4^{3-}$/l on average.

| No | Average peak high (cm) | Total phosphate concentration (mg/l) |
|----|------------------------|-------------------------------------|
| 1  | 0.15                   | 0.480                               |
| 2  | 0.14                   | 0.448                               |
| 3  | 0.13                   | 0.416                               |
| 4  | 0.13                   | 0.416                               |
| 5  | 0.12                   | 0.384                               |
| 7  | 0.14                   | 0.448                               |

Average ($\bar{x}$) 0.430
Standard deviation (s) 0.029
% RSD 6.728
3.5. Total phosphate determination of artificial sample (0.5% detergent solution) using UV radiation destruction method

An artificial sample, made from 5 grams of detergent dissolved in 1000 ml of demineralized water, was used in this study. Prior to the determination, sulfuric acid, potassium peroxodisulphate and artificial sample were mixed thoroughly in the mixing chamber, then flowed into a heating chamber (60°C) at the flow rate of 3 ml/min. Afterwards, the sample was injected to the oxidation reactor (UV radiation) connected to the Segmented Flow Analysis equipment.

Table 3. Results of total phosphate analysis from artificial sample (0.5% detergent solution) using oxidation reactor (UV radiation).

| No. | Average peak high (cm) | Total phosphate concentration (mg/l) |
|-----|------------------------|-------------------------------------|
| 1   | 8.6                    | 5.3636                              |
| 2   | 9                      | 5.4363                              |
| 3   | 9.8                    | 5.5818                              |
| 4   | 9.8                    | 5.5818                              |
| 5   | 11.1                   | 5.8182                              |
| 6   | 8.7                    | 5.3818                              |
| 7   | 11.3                   | 5.8545                              |
| 8   | 9.7                    | 5.5636                              |
|     | Average (x̄)            | 5.5727                              |
|     | Standard deviation (s) | 0.1830                              |
|     | % RSD                  | 3.2839                              |

Table 3 shows that the phosphate concentration (PO₄³⁻) obtained was 5.5727 mg-PO₄³⁻/l and the relative standard deviation value was 3.28%. The relative standard deviation obtained by the oxidation (UV radiation) method was still below 5%, which shows the repetition of the method is quite good [12].

Table 4. Percentage of recovery of total phosphate from artificial sample (0.5% detergent solution) after the oxidation process using UV radiation.

| No. | Phosphate standard solution addeda (mg/l) | Artificial sample with phosphate standard solution added (mg/l) |
|-----|------------------------------------------|---------------------------------------------------------------|
| 1   | 1.20                                     | 6.6545                                                       |
| 2   | 1.20                                     | 6.6909                                                       |
| 3   | 1.20                                     | 6.7455                                                       |
| 4   | 1.20                                     | 6.6909                                                       |
| 5   | 1.20                                     | 6.6545                                                       |
| 6   | 1.20                                     | 6.7818                                                       |
| 7   | 1.20                                     | 6.6909                                                       |
| 8   | 1.20                                     | 6.7455                                                       |
|     | Average (x̄)                             | 6.7068                                                       |
|     | Standard deviation (s)                   | 0.0459                                                       |
|     | % RSD                                    | 0.6844                                                       |
|     | % Recovery                               | 94.51 %                                                      |

a Standard solution of 120 mg-PO₄³⁻/l (1 ml) was each transferred into the 8 volumetric flasks respectively and then diluted with 0.5% detergent solution to 100 ml. The average total phosphate concentration of 0.5% detergent solution was 5.5727 ± 0.1830 mg/l.
3.6. Percent recovery determination of UV radiation destruction method from artificial sample (0.5% detergent solution)

Recovery value indicates the accuracy of the method. Accuracy is an indication that shows the degree of results closeness of the determination to the actual levels of analyte. In this experiment, the recovery obtained was 94.51 % (Table 4).

3.7. Destruction method using oxidation reactor (UV Radiation)

According to Turner [3], it is estimated that around 50-75% of the phosphate compounds present in lakes, reservoirs, and rivers come from detergent waste. Based on this and the good recovery value from destruction method, the method was then used for the determination of phosphate in the water samples from Cikapundung and Citarum Rivers.

| No | Average peak high (cm) | Total phosphate concentration (mg/l) |
|----|------------------------|-----------------------------------|
| 1  | 4.0                    | 4.5273                            |
| 2  | 4.0                    | 4.5273                            |
| 3  | 5.8                    | 4.8545                            |
| 4  | 4.8                    | 4.6727                            |
| 5  | 4.1                    | 4.5454                            |
| 6  | 3.9                    | 4.5091                            |
| 7  | 3.7                    | 4.4727                            |
| 8  | 3.9                    | 4.5091                            |
|    | Average (\(\bar{x}\)) | 4.5773                            |
|    | Standard deviation (s) | 0.1356                            |
|    | % RSD                  | 2.9624                            |

| No | Average peak high (cm) | Total phosphate concentration (mg/l) |
|----|------------------------|-----------------------------------|
| 1  | 2.2                    | 4.2000                            |
| 2  | 2.1                    | 4.1818                            |
| 3  | 2.2                    | 4.2000                            |
| 4  | 1.8                    | 4.1273                            |
| 5  | 2.2                    | 4.2000                            |
| 6  | 2.3                    | 4.2182                            |
| 7  | 2.3                    | 4.2182                            |
| 8  | 1.8                    | 4.1273                            |
|    | Average (\(\bar{x}\)) | 4.1841                            |
|    | Standard deviation (s) | 0.0361                            |
|    | % RSD                  | 0.8628                            |

Total phosphates analysis using this method gave the average phosphate content of 4.5773 mg-PO\(_4\)\(^3-\)/l for Cikapundung River and 4.1841 mg-PO\(_4\)\(^3-\)/l for Citarum River (Table 5 and 6). The high phosphate concentration was caused by the turbulence of river flow and stirring of the water mass which lead to elevating of the phosphate-containing compounds at the bottom of the river and rising to the
surface [10]. Phosphate concentration in Cikapundung River water was found to be higher than the Citarum River water; this is because the wastewater stream in the Cikapundung River is greater than Citarum. The data suggest that both rivers from where the samples were taken for this study had been eutrophic. Eutrophication is water pollution caused by excessive nutrients in the water ecosystem. Water is classified as eutrophic when phosphate concentration is in the range of 0.035–0.1 mg-PO₄³⁻/l [11].

4. Conclusion
This experiment shows that oxidation reactor (UV radiation) combined with a solution of warm potassium persulfate can be used for total phosphate determination, especially for samples containing detergents. It can be noted that the sample preparation method using oxidation reactor (UV radiation 325 nm), which was developed in our laboratory, gave very good results with the percentage of recovery at 94%.

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