

Determination of the Total Phosphorous Using a Non-Segmented Biphasic Flow (NSBF) Injection

Alexandre Correa de Lima¹, Astréa F. de Souza Silva² and Andre Fernando Oliveira^{2*}

1-Núcleo de Ciências Ambientais, Universidade de Mogi das Cruzes, Av. Cândido X. A. Souza, 200, Mogi das Cruzes, São Paulo, Brazil 08717-460; 2- Departamento de Química – Universidade Federal de Viçosa, Av. P.H.Rolfs s/n Viçosa, Minas Gerais, Brazil 36570-000. andref.oliveira@ufv.br

Abstract

The Non-Segmented Biphasic Flow System (NSBF) was applied in total phosphorous determination. The oxidation was performed in a reaction coil heated by electrical resistances. The high efficiency of heating in such system allows the simultaneous formation of liquid and vapor phases without segmentation. This unusual condition has reduced the hydrodynamic pressure and thus providing good work conditions. The system was based on the organic matter oxidation by persulfate in acid medium. The phosphomolybdic acid-green malachite ion-association was spectrophotometrically quantified in 650 nm. The analytical range was from 26.0 µgP.L⁻¹ to 320 µg P.L⁻¹ and a limit of detection of 9 µgP.L⁻¹ was obtained, with an analytical sensitivity of 0.27 L.mg⁻¹. The analytical frequency was 40 samples per hour with a repeatability of 4.7% (n = 10).

Keywords Total Phosphorous Determination; Non-segmented Biphasic Flow; Motomizu reagent; on-line persulfate oxidation

1. Introduction

The phosphorous is an important element in vital molecules such as nucleic acids, myo-inositol, ATP, *etc.*. Usually, this element is considered a limiting nutrient for phytoplankton growth in aquatic system. Hence, large quantities of phosphorous in water are the main factor for eutrophization in lakes and rivers. For these reasons, the determination of total phosphorous is essential to limnological studies [1].

The total phosphorous methods are usually based on off-line oxidation and require a long-term analysis [2-4]. On-line digestion methods were proposed using microwave oven as a heating source [5] but the production of bubbles is a great trouble in the repeatability due a transient signal [6] distortion. These systems have high electric power consumption.

The NSBF (non-segmented biphasic flow) was proposed by Oliveira & Fatibello in 2000 [7], showing a high heating efficiency. This method is based on the formation of two continuous phases: liquid and vapor with especial characteristics: a narrow flow of liquid streams on the internal walls of the tube while the vapor flow fills the rest of the tube. Therefore does not occur segmentation by bubbles differently from others flow injection with heating system.

In the NSBF system previously proposed, the reaction coil was positioned directly on the short antenna of magnetron of a domestic microwave oven. This assemble allowed the increase in efficiency of the endothermic reaction, beyond breaking the paradigm of the limit temperature of 40°C, once it operates at boiling point of solution without creating distortions of signal[5]. Furthermore, a continuous system for absorption of radiation excess was developed to avoid overheating the device

Unfortunately, the use of microwave oven for flow injection system has serious disadvantages: the large physical space and a high waste of energy due to the low efficiency of the magnetron (65% ca.) and finally, the excess of microwave energy released (once only a few watts are absorbed by the coiled reactor whereas about 700W are liberated by the oven). Although the new separation chamber [8] dispenses water refrigeration for a reaction coil, it is necessary for two

attenuators (dummy loads with 500 mL each) used for absorbing excess microwave radiation, and then, increasing complexity and water consumption.

In this work, a new NSBF system was used to determine the total phosphorous in water. The microwave oven was substituted for electric resistance with low electric power, keeping the high efficiency of heating. The system size and electric energy consumption decreased and refrigeration with water was not necessary.

2 Experimental

2.1. Reagents

All solutions were prepared with water purified in a Master System - Gehaka (São Paulo, Brazil) and all reagents used were from an analytical reagent grade. Stock solutions of potassium persulfate (Aldrich) at 15% (m/V); silver nitrate (Carlo Erba) 50 mmol.L⁻¹; phytic acid (Acros) 100 mg P.L⁻¹; and dihydrogen phosphate (F. Maia) 100 mg P/L: were prepared. Silver acid solution: suitable volumes of concentrated nitric acid (Synth) and stock solution of silver nitrate were mixed and diluted to 100.0 mL with water. Chromogenic Reagent (Motomizu's Reagent)[9,10] 20.0 g of ammonium molybdate (NH₄Mo₆O₂₄·4H₂O) and 92.0 mg of malachite green oxalate (Nuclear) were dissolved in 500.0 mL of water. 250.0 mL of absolute ethanol (F. Maia) and 70.0 mL of concentrated sulfuric acid (F. Maia) were added under constant agitation. The volume completed to 1000.0 mL after the total dissolution of the reagents, otherwise, the solution would be unstable with the precipitation of some reagents;

2.2. Apparatus

The flow injection manifold is shown in Figure 1. All flow tubes used were 0.8 mm i.d. PTFE. The propulsion of fluids was done with an eight-channel Ismatec (Zurich, Switzerland) Model IPC-8 peristaltic pump supplied with Tygon pump tubes. Two aquarium 50W electric resistors (Master, São Paulo, Brazil) were used for the heating unit, or NSBF coil (100 cm each), and the flow tubes were coiled around these resistors.

The different level of electric power was obtained by alternating the power supply (110 or 220V) in each resistor. So, a total power of 100W was obtained, with step of 25W.

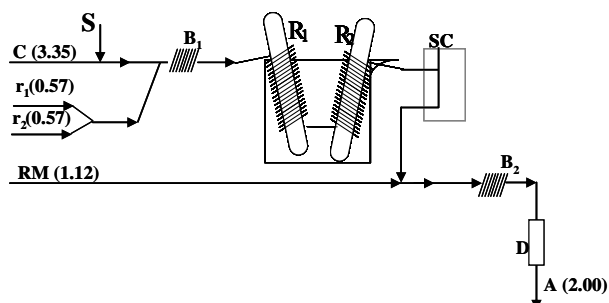


Figure 1 Schematic diagram of NSBF-FI. (C) water carrier, (S) sample loop; (r_1) potassium persulfate, (r_2) acid reagent, (RM) Motomizu's reagent, (R_1 and R_2) aquarium electric resistance, (SC) separation chamber, B_1 (50 cm) and B_2 (25cm) coil reactors, (D) detector ($\lambda = 650$ nm), (A) suction flow to waste reservoir. The optimum flow rate is in parenthesis ($\text{mL}\cdot\text{min}^{-1}$).

The homemade separation chamber is built in acrylic. The vapor phase was liberated in the bottom of the chamber. Furthermore, an acrylic box (200mm x 100mm x 100mm) was used to contain this chamber and to condense the liberated vapor and the naturally condensed vapor was drained to waste.

Spectrophotometric measurements were carried out in a Micronal (São Paulo, Brazil) B474 with a glass flow cell.

An aliquot of 250 μL sample/reference solution was inserted in a carrier flow and merged with r_1 (persulfate solution) and r_2 (acid reagent: silver ion (catalyst) in acid solution). The zone sample was pumped to the heating unit (NSBF unit) and two non-segmented phases (liquid and vapor) were formed. After the oxidation of organic material, both phases merged with the Motomizu's Reagent (MR), and the ion association of phosphomolybdic acid and malachite green oxalate was aspirated into the detector.

Samples used for comparison were collected in Tietê river near Mogi das Cruzes town (São Paulo, Brazil).

3. Results and Discussion

3.1 Procedure for system's evaluation

The method was optimized by searching for the maximum analytical sensitivity curve and oxidation efficiency.

The sensitivity of the spectrophotometric method is the ratio between analytical response (absorbance) and analyte concentration. Nevertheless, the analyte is not, necessarily, the chromophore specie (CE), which, in fact, absorbs the radiation. Thus, the sensitivity can be related to Beer-Lambert-Bouguer law through Equation 1, where ' r ' is molar ratio between CE and analyte concentrations; ' ϵ ', molar absorptivity of CE and ' f ' a global efficiency of chemical reaction and dil is a dilution factor.

$$S = \frac{\epsilon \cdot r \cdot f}{dil} \quad \text{Equation 1}$$

Therefore, the oxidation efficiency was defined, in each operational condition, using the sensitivities of phytic acid and phosphate (Equation 2). The phytic acid was chosen as organophosphate due to its high resistance to oxidation⁷. The

phosphate was produced in oxidation of organophosphate and reacted with the Motomizu reagent.

$$f = \frac{S(\text{phytic acid})}{S(\text{phosphate})} \quad \text{Equation 2}$$

3.2. Study of chemical parameters

The influence of persulfate [7-9] on oxidation of organic matter was studied (Figure 2). Concentration of phytic acid and phosphate varied from 8 μg P/L to 250 μg P/L.

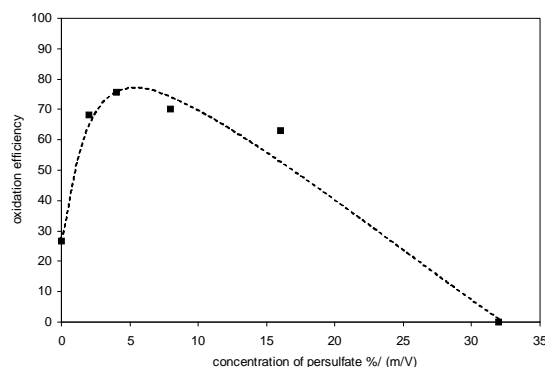


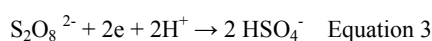
Figure 2 - Influence of persulfate concentration on the efficiency of oxidation. r_1 , 4% (w/v) potassium persulfate; r_2 2.0 $\text{mmol}\cdot\text{L}^{-1}$ silver ion in 0.2 $\text{mol}\cdot\text{L}^{-1}$ nitric acid; FBNS power: 75W, sample loop: 250 μL , (\square) phytic acid, (\blacksquare) phosphate.

The oxidation efficiency improved with the increase of the persulfate concentration up to 4% (m/v) and decreased for high concentrations. This result can be explained by the oxidation of Motomizu's reagent by residual persulfate, once the phosphate sensitivity also decreases with the increase of persulfate concentration in the medium (Figure 3) The destruction of reagent by oxidant agent was also observed by Benson *et al.*[11]. In this way, persulfate 4%(m/v) was selected for other studies.

In this condition, the oxidation efficiency was linearly increased from 30% to near 100% with resistance power from 0 to 75W. The NSBF was not obtained at 100W, due high evaporation rate and bubble formation on detector. The increase of resistance power is favorable to oxidation of organic matter.

The increase of acidity on r_2 reagent can enhance the oxidation efficiency significantly from 76% to 97%, in concentration range from zero to 0.094 $\text{mol}\cdot\text{L}^{-1}$ HNO_3 , in presence of 2.0 $\text{mmol}\cdot\text{L}^{-1}$ of silver ion. For higher concentration, the sensitivity of phosphate decreases again. (Figure 4).

It is explain by increase of acidity increases the sulphate protonation (pK_2 equal to 2.12) dislocating the persulfate reduction semi-reaction. (Equation 3)



The formation of NSBF depends on both, total flow rate and electrical power of the resistors. So, the two phases separation (NSBF formation) occurred with 25W, with flow rate from 0.5 mL/min . Therefore, the behavior of the system at different heating rates was studied.

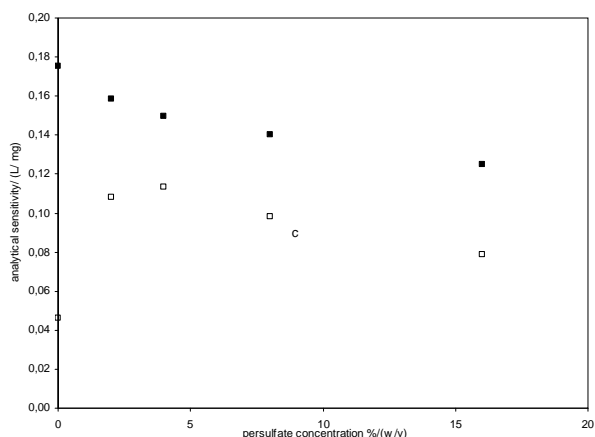


Figure 3 – Effect of persulfate concentration on analytical curve sensitivity. Loop sample: 250 μL . (\square) phytic acid, (\blacksquare) phosphate. (same conditions of Figure 2)

The oxidation efficiency increases linearly from 26% up to 95% at 75W when the solvent evaporation rate is so high that aspiration of the liquid into the detector is not possible without bubble segmentation.

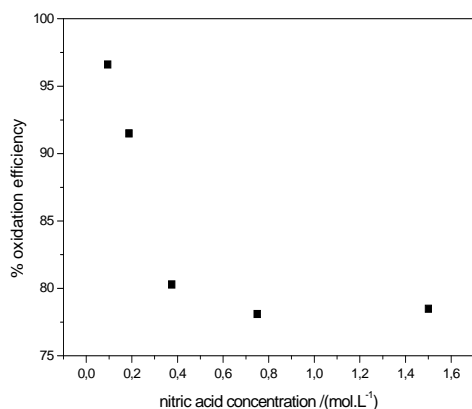


Figure 4 – Influence of acidity on sensitivity of the analytical curve. r_1 , 4% (w/v) potassium persulfate; r_2 : 2,0mmol/L silver ion in nitric acid; FBNS power: 75W, sample loop: 250 μL .

The evaporation rate in the NSBF, residence time of sample zone and the natural re-sampling in the separation chamber were influenced the total system flow rate. In this system, the total system flow rate and the aspiration rate were controlled by the same peristaltic pump. So, the total flow rate was studied from 1,1 to 9,0 $\text{mL}\cdot\text{min}^{-1}$ (Figure 5). The ration between individual channels of r_1 , r_2 and carrier was kept constant as in polyvalente system[12].

The total system flow rate obtained was 4.5 $\text{mL}\cdot\text{min}^{-1}$. In lower flow rate is a high residence time causing a the high heat rate which increases the malachite green oxidation, what diminishes the orthophosphate sensitivity. Besides, a small internal volume of chamber separation decreased the mixing-chamber effect, when compared to the literature[9].

The catalytic action of the silver ion was studied. A 100% oxidation efficiency with 3.1 $\text{mmol}\cdot\text{L}^{-1}$ of the silver ion was obtained. Nevertheless, $\text{Ag}(\text{II})$ formed in the presence of persulfate, acts as intermediary. The concentration of silver ion above 3.1 $\text{mmol}\cdot\text{L}^{-1}$ reduces the oxidation efficiency, due, again, to the increase of malachite green oxidation or silver

phosphate formation.

3.3 Characterization of the proposed system

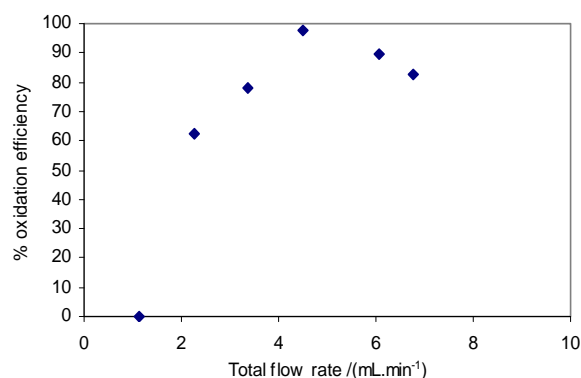


Figure 5 – Influence of total system flow rate on oxidation efficiency. r_2 : 2,0 $\text{mmol}\cdot\text{L}^{-1}$ silver ion in Nitric acid 0.094 $\text{mol}\cdot\text{L}^{-1}$, potassium persulfate 4% (w/v), Electrical power 75W and 250 μL sample volume.

The figures of merit were available under the optimum conditions: 4.0%(m/v) potassium persulfate; 3.1 $\text{mmol}\cdot\text{L}^{-1}$ silver ion; 0.094 $\text{mol}\cdot\text{L}^{-1}$ nitric acid; electrical power of 75W and 250 μL sample/reference solution loop;

The analytical range was from 26.0 $\mu\text{gP}\cdot\text{L}^{-1}$ to 320 $\mu\text{gP}\cdot\text{L}^{-1}$ with a limit of detection (3σ) of 9.0 $\mu\text{gP}\cdot\text{L}^{-1}$, available with the standard deviation of blank in the analytical curve [13].

The accuracy was available through a comparison method using samples from the Tietê river from Mogi das Cruzes town (São Paulo, Brazil). The proposed method was compared with a batch method with Motomizu reagent and closed-vial microwave-oven irradiation (Figure 6).

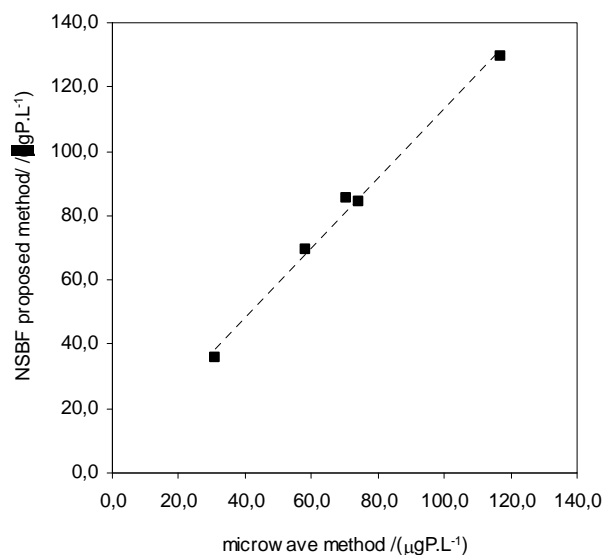


Figure 6 – Comparison of proposed NSBF method and closed-vial microwave-oven method.

The correlation between these two methods was good with a determination coefficient (r^2) of 0.993 ($n=5$). The slope does not differ significantly from one unit and only a small additional deviation of 5.0 $\mu\text{g}\cdot\text{L}^{-1}$ was observed. The repeatability of signal was 4.7% ($n=9$) for 100 $\mu\text{gP}\cdot\text{L}^{-1}$ phytic

acid.

4. Conclusions

The NSBF system was successfully applied for the determination of the total phosphate with persulfate in water from rivers. The use of electrical resistors was enough to generate the NSBF, considerably reducing the physical space used by the FIA system as well as the electrical energy consumption. A good repeatability and a detection limit of 9µg P/L was obtained.

5. References

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