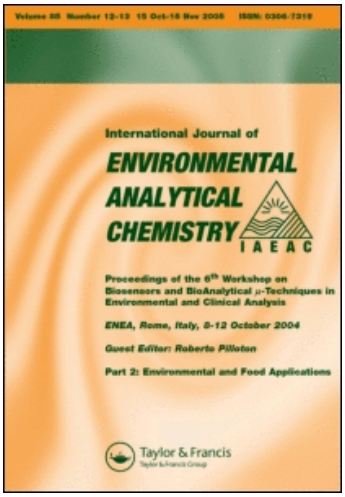

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Direct Determination of Particulate Phosphorus in Water With Perchloric Acid Digestion of Whole Membrane Filters

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DIRECT DETERMINATION OF PARTICULATE PHOSPHORUS IN WATER WITH PERCHLORIC ACID DIGESTION OF WHOLE MEMBRANE FILTERS

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Particulate phosphorus is recovered from a water sample on a cellulose nitrate membrane filter which is then dissolved in perchloric acid and digested at 170°C overnight. The released orthophosphate is determined without neutralization by the phosphomolybdate blue method of Murphy and Riley (1962). The method can be applied to the amounts of phosphorus retained on the filter ranging from 0.4 to 25 µg.

KEY WORDS: Particulate phosphorus, photometric determination, membrane filter, perchloric acid digestion, water.

INTRODUCTION

Particulate phosphorus (PP) is most frequently quantified as the difference between the values of total phosphorus (TP) and total dissolved phosphorus (TDP)[1,2,3]. Direct determination is required when concentrations of PP are so low that a sufficient precision cannot be obtained by the difference method. In this case, PP is recovered from a water sample on a membrane filter, and together with the filter, is digested by HNO_3 followed by $HClO_4$[2] or by $K_2S_2O_8$ and $HClO_4$[3], in order to oxidize organic matter and release phosphorus as orthophosphate. Alternatively, the sample is passed through a membrane filter coated with a little magnesium carbonate, which is subsequently washed out from the filter; and the obtained suspension is then digested by perchloric acid[4]. Both methods, however, require a laborious procedure of neutralization before colour development.

This paper describes a simple test-tube procedure for directly determining PP concentrations on cellulose nitrate membrane filters which does not require neutralization. The method is based on the semi-micro determination of TP with perchloric acid digestion[5] and uses also the same reagents and the same optimized conditions for hydrolysis and colorimetry. The

digestion conditions, however, had to be modified to achieve complete oxidation of organic matter from the particulate material and the filter.

EXPERIMENTAL

Materials, equipment and reagents

Membrane filters Synpor 6 (cellulose nitrate, product of Barvy a laky s. p., Praha, Czechoslovakia) with 0.40 μm nominal pore size and a diameter of 3.5 cm were used in the separation of PP. To minimize blank values, filters were repeatedly washed in hot distilled water (25 filters per 1 liter, 10 minutes at ca 90°C, three times). The filtration pressure used in filtering the samples was less than 25 kPa. Filters with retained particulate matter were dried and stored before analysis at laboratory temperature for periods ranging from one day to six months.

Other materials, glassware, digestion block and reagents were used as described in ref. 5.

Procedure

The filter containing particulate matter was placed in an open test tube, dissolved in 1.2 ml of 3.3 M $HClO_4$ (115°C, 2–3 hours) and digested at 170°C overnight (10–15 hours). In the morning (or just after decolouration of perchloric acid), the sample was diluted with 20 ml of redistilled water, mixed thoroughly and hydrolyzed in the stoppered test tube (100°C, 60 minutes). After cooling to room temperature and mixing the sample again, 10 ml of it were transfered to another test tube and 1 ml of mixed reagent I[5] and 1 ml of mixed reagent II[5] were added to the second and the first test tubes, respectively. PP was calculated similarly as in the original method[5] using absorbances corrected for turbidity.

RESULTS AND DISCUSSION

Digestion

In comparison with the TP method[5], the prolonged heating and the oxidation of greater amount of organic matter increased the loss of the original acidity of the digested sample to about 20%. To compensate for the loss, the amount of perchloric acid used in the digestion step was increased to maintain the optimum values of the H^+ concentration and the$[H^+]/[Mo(VI)]$ ratio in the colorimetric step[5,6,7,8].

Table 1 Comparison of methods for PP determination.

SAMPLE	*TP-TDP*[a]	*PP*[b]		*IS*[c]
	[µg.l^{-1}]	*[µg.l^{-1}]*	*[µg per filter]*	*[%]*
RIVERS:				
1	66.7 ± 1.0	67.7 ± 1.8	3.4 ± 0.09	93
2	76.9 ± 2.8	72.5 ± 1.5	7.3 ± 0.15	95
FISH PONDS:				
1	42.8 ± 0.6	43.5 ± 1.9	4.4 ± 0.19	99
2	68.7 ± 1.2	74.0 ± 1.3	7.4 ± 0.13	109
RESERVOIRS AND LAKES:				
1	12.2 ± 0.5	14.1 ± 0.3	3.5 ± 0.07	97
2	19.3 ± 1.7	20.7 ± 0.3	4.1 ± 0.06	102
3	37.9 ± 0.6	39.1 ± 0.6	9.8 ± 0.15	98
4	30.2 ± 0.2	30.9 ± 0.7	3.1 ± 0.07	102
OTHERS:				
1[d]	329 ± 1.7	350 ± 5.5	7.0 ± 0.11	100

[a] difference between TP and TDP; mean ± standard deviation (n = 4)
[b] proposed direct method; mean ± standard deviation (n = 5)
[c] recovery of internal standard in the direct method; means of duplicate analyses
[d] suspension of algae (*Chlorella sp.*)

Range of determination, precision and accuracy

The detection limit was estimated as the sum of the mean value of the blanks plus three times the mean value of sample standard deviations (SD). The mean value of the blank from duplicate determinations in 15 different series was 0.042 ± 0.020 µg P per filter Synpor 6 (mean ± SD). The average sample SD from the analysis of 9 samples analyzed in 5 parallel determinations (Table 1) was 0.110 µg P. Thus, the detection limit was $0.042 + 3 \times 0.11 = 0.372$ µg P retained on the membrane.

The upper limit of the method (25 µg P per filter) is restricted by the concentration of Sb(III) in the colorimetric step. The calibration is linear up to the ratio of $[PO_4^{3-}]/[Sb(III)] = 0.5$; at higher values a breakage occurs on the calibration curve.

The precision, estimated as the mean value of the relative SD of 9 samples from Table 1, was 2.0% for the range from 3.1 to 9.8 µg PP retained on the filter.

The accuracy of the proposed method was tested by adding a known concentration of KH_2PO_4 (2 µg P per sample) to 9 samples (Table 1) as internal standards and to 15 blanks as external standards. The percent recovery of P for internal standards was 99.6 ± 4.4 (mean ± SD). The relative SD calculated for external standards was 4.7%.

Comparison

The proposed direct method was compared with results obtained by calculating the difference between TP and TDP values determined with the semi-micro method[5]. The comparison was performed on a set of 9 samples of different types (Table 1), analyzed in 5 parallel determinations, and on a set of 40 samples from rivers (20 samples; 6–162 µg PP.l^{-1}) and

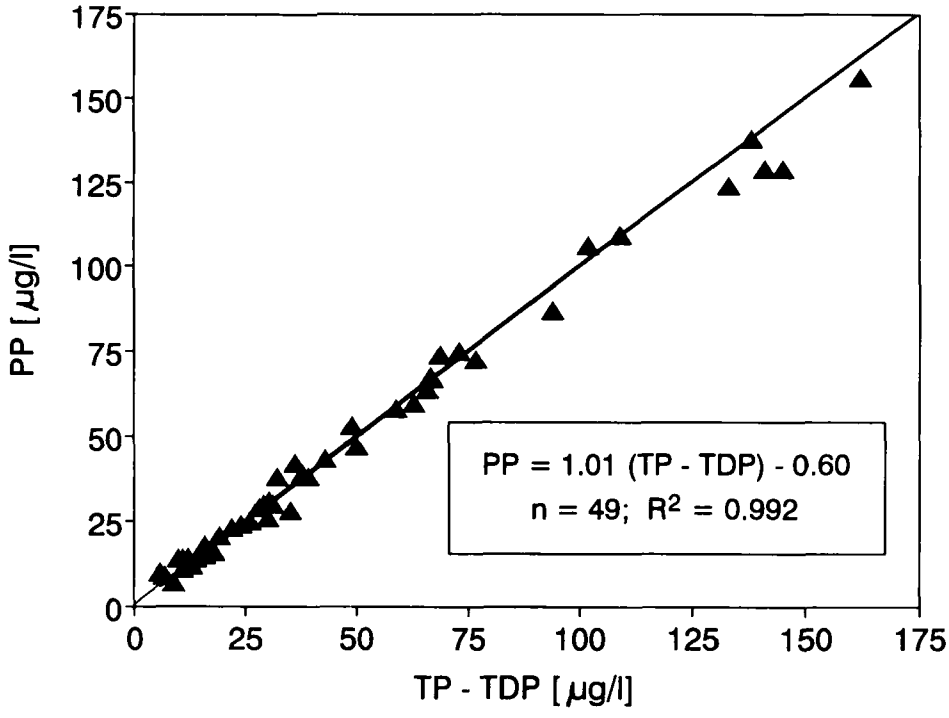

Figure 1 Comparison of PP determination on filters (PP) with the difference method (TP-TDP) for 49 samples of water collected from rivers, reservoirs and lakes.

reservoirs or lakes (20 samples; 7–63 µg $PP.l^{-1}$) analyzed in 2 parallel determinations. The linear regression analysis calculated for the total 49 samples of both sets revealed satisfactory linearity between the methods (Figure 1). Likewise, no significant difference was found between the methods using the paired t-test. Computed t statistic was 0.277 and significance level $\alpha = 0.79$ for all 49 samples.

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