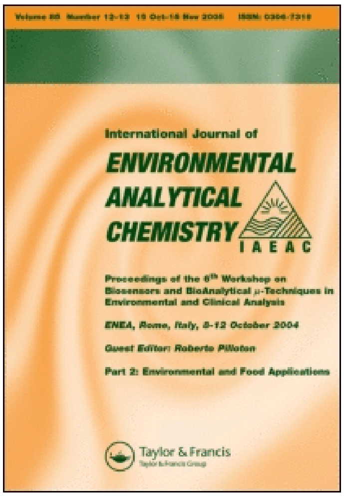

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Total Phosphorus Analysis of Wastewater Samples using the Stannous Chloride Reduction Procedure

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Total Phosphorus Analysis of Wastewater Samples using the Stannous Chloride Reduction Procedure

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The stannous chloride reduction procedure for the colorimetric determination of total phosphorus in wastewater samples using potassium persulphate digestion was evaluated. Samples with salinities as low as 50 mg/l gave phosphorus levels approximately 10% lower than the true levels when absorbance readings were taken after the recommended time interval of 10 minutes. With increasing salinity, the error increased to approximately 20%. This error can be overcome by the addition of sodium chloride to both standards and samples to achieve salinity levels of 2,000 mg/l or greater, and making absorbance measurements after allowing at least 2 but not more than 3 minutes for colour development.

KEY WORDS: Phosphorus, analysis, wastewater.

INTRODUCTION

Phosphorus reaches natural waters from many sources. A major source is sewage and sewage effluents where the input from phosphates incorporated in synthetic detergents is considerable. As phosphorus is an essential nutrient in the eutrophication process, accurate methods of analysis are important in water pollution studies.

A number of procedures for the determination of phosphorus in waters have been described.[1,2] These procedures rely on the conversion of the various forms of phosphorus to orthophosphate which is then measured. For the determination of total phosphorus, organic phosphorus compounds are oxidised, and condensed phosphates hydrolysed to orthophosphate which is measured with the orthophosphate already present. Of a number of oxidising agents, potassium persulphate is perhaps the most suitable,[3–5] although some deficiencies have been reported.[6,7]

The measurement of orthophosphate involves two stages. Firstly, molybdophosphoric acid is formed from the orthophosphate and ammonium molybdate under acidic conditions. The molybdophosphoric acid is subsequently reduced to a blue complex, molybdenum blue, which is determined colourimetrically. A number of reducing agents have been utilised in this step,[2] with ascorbic acid and stannous chloride the most commonly accepted.

The stannous chloride reduction procedure has been extensively evaluated in seawater and the effect of a salinity interference is well known.[8–11] However, little has been published on the application of this procedure to freshwaters and wastewaters of low salinities, although interferences leading to low results have been reported in the analysis of sewages for phosphate.[5] The procedure of Gales *et al*,[12] utilising a persulphate digestion, was evaluated for the determination of total phosphorus in wastewater samples. It is considered that the procedure is comparable to that described in *Standard Methods for the Examination of Water and Wastewater*,[1] in which a neutralisation step has been introduced. In both procedures the final acid concentrations are very similar (0.16 and 0.19 M respectively) while the concentrations of other reagents are the same.

EXPERIMENTAL

The reagents used were identical to those specified by Gales *et al.*[12]

Dilute sulphuric acid

Concentrated sulphuric acid (310 ml) was carefully added to about 500 ml water and on cooling, made up to 1 litre.

Ammonium molybdate solution

Ammonium molybdate (25 g) was dissolved in 175 ml water. Concentrated sulphuric acid (77.5 ml) was carefully added to 400 ml of water and the solution cooled. The two solutions were mixed and made up to 1 litre.

Stannous chloride solution

Stannous chloride dihydrate (2.5 g) was dissolved in 100 ml glycerol. Warming was necessary to effect solution.

PROCEDURE

Aliquots of the standards or samples were diluted to approximately 50 ml in Erlenmeyer flasks. Potassium persulphate (0.40 ± 0.01 g) and dilute sulphuric acid (1.0 ml) were added. The mixture was then boiled on a hot plate for 45 minutes, distilled water being added where necessary to prevent boiling to dryness. The digestates, after cooling, were made up to 50 ml in volumetric flasks which had sufficient room above the mark to accommodate the reagents (2.0 ml). Colour development was achieved by adding the ammonium molybdate solution (2.0 ml), mixing well, followed by the stannous chloride solution (3 drops) and again mixing well. Absorbance measurements were made at 650 nm on a Pye Unicam SP6-300 spectrophotometer using a 1 cm flow-through (autocell) accessory. The spectrophotometer was zeroed on distilled water. Blanks were also carried out but were insignificant.

STANDARDS

Potassium dihydrogen phosphate (BDH Chemicals AnalaR reagent) and adenosine-2′-(3′)-monophosphoric acid (BDH Biochemicals) were used as the inorganic orthophosphate and organic phosphate standards respectively.

RESULTS AND DISCUSSION

Digestion

Aliquots containing 20 μg inorganic orthophosphate phosphorus were digested for various times, and the absorbances measured after exactly 10 minutes for colour development, the recommended time period[12] (Table I).

TABLE I

Absorbance after 10 minutes for colour development versus digestion time for 20 μg inorganic orthophosphate phosphorus

Digestion time (mins)	Absorbance[a]	Standard deviation
10	0.177	0.030
20	0.300	0.011
30	0.314	0.005
45	0.321	0.002
60	0.320	0.004
90	0.320	0.005

[a] Average of 5 replicates.

These results show that residual potassium persulphate interferes in the analysis by lowering the absorbance, the phosphorus being already present in the reactive orthophosphate form. The results also indicate that 45 minutes are required to decompose all potassium persulphate. Gales *et al*[12] reported that any traces present after 30 minutes do not affect the results, however, this study shows a slightly lower absorbance in comparison with longer digestion times.

More importantly, these results also show it is not possible to differentiate between the progress of oxidation of organic phosphorus compounds to orthophosphate, and decomposition of the potassium persulphate. The increase in absorbance with increasing digestion time with organic phosphorus compounds has been interpreted in terms of extent of digestion,[6,12] whereas this may not be so. The quantity of potassium persulphate used was found not to be critical as identical results were obtained with 0.3 or 0.5 g quantities.

The persulphate oxidation procedure was investigated with adenosine -2'-(3')-monophosphoric acid. Replicate solutions of this compound containing 20 μg phosphorus were analysed using 0.40 ± 0.01 g potassiun persulphate, with a recovery of 93 ± 2%. Thid recovery was considered to be acceptable as the material used was not of analytical reagent grade.

It is doubtful though how data obtained with some organic phosphorus compounds relate to real samples, e.g. adenosine -2'-(3')-monophosphoric acid is no doubt hydrolysed rapidly. Since the nature of organic phosphorus in wastewaters is not well understood, it is thus difficult to test digestion efficiencies on the types of organic compounds found in wastewaters.

Various dilutions of sewage were digested with 0.40 g potassium persulphate for 45 minutes and the colour development monitored as a function of time (Figure 1). The absorbance readings, both maxima, and after 10 minutes for colour development as a function of dilution are shown in Figure 2. The phosphorus levels obtained for the original samples are identical if the absorbance maxima are used to calculate these results. In contrast, the absorbance readings taken after 10 minutes for colour development yield decreasing phosphorus levels with increasing amounts of sewage in the sample analysed. The use of absorbance readings, taken after the recommended time period of 10 minutes, could incorrectly infer that incomplete oxidation has occurred with increasing concentration of sample rather than an interference phenomenon indicated by these results.

It would appear that 0.4 g potassium persulphate is sufficient to oxidise the organic phosphorus present to orthophosphate since the same initial phosphorus concentrations are obtained from the various dilutions. Forty-five minutes would also appear to be sufficient digestion time as results obtained with longer times were identical.

Colour development behaviour

The colour development with inorganic orthophosphate standards, with and without digestion, i.e. with no added persulphate or heating, was investigated using the procedure described under "Experimental" with a digestion time of 45 minutes. The results obtained without digestion are shown in Figure 3. With digestion, behaviour was essentially the same except that absorbances at any time were about 10% lower for a given phosphorus level. Thus sulphate formed in the decomposition of the persulphate oxidant reduces the colour intensity but has little effect on the rate of colour development and subsequent fading. This shows standards must be carried through the digestion procedure.

These results indicate that the orthophosphate phosphorus level itself influences the colour development and fading behaviour. As the level increases, the maximum colour intensity is reached faster and persists for a shorter period of time, i.e. the colour fades more

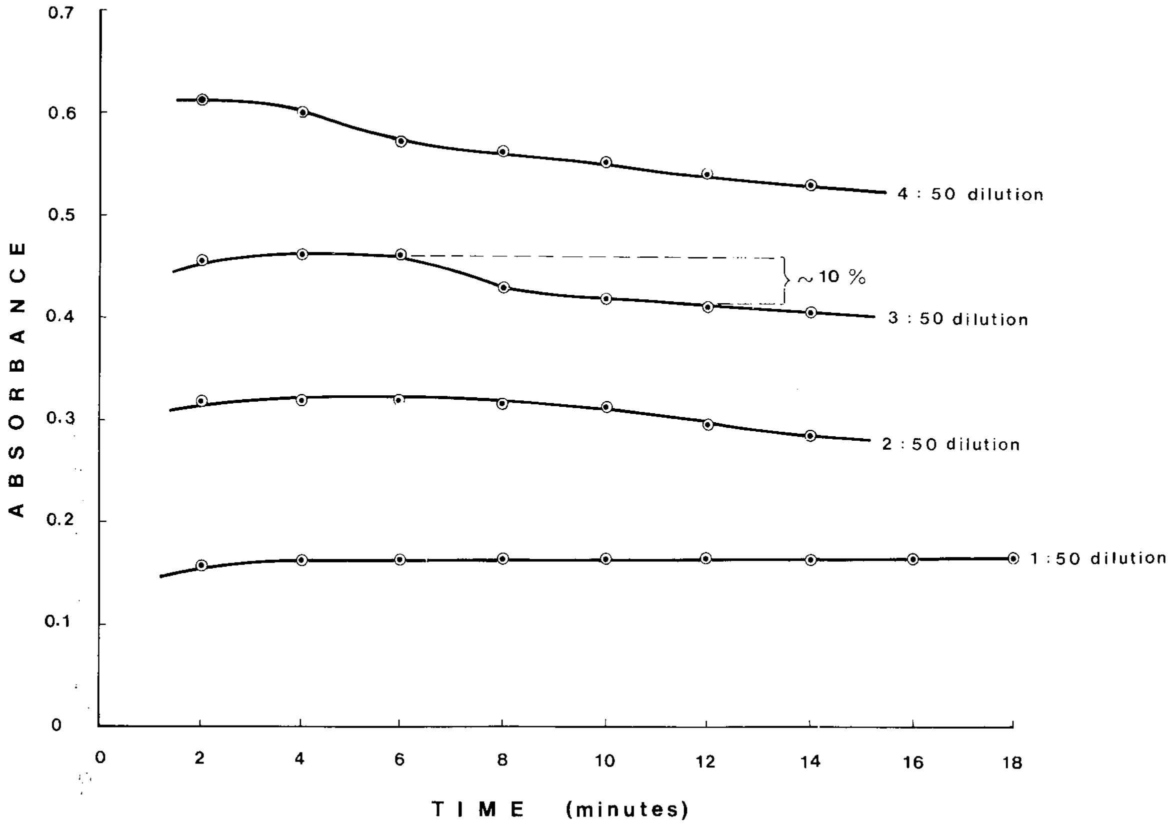

FIGURE 1 Colour development (absorbance versus time) with various dilutions of sewage after persulphate digestion.

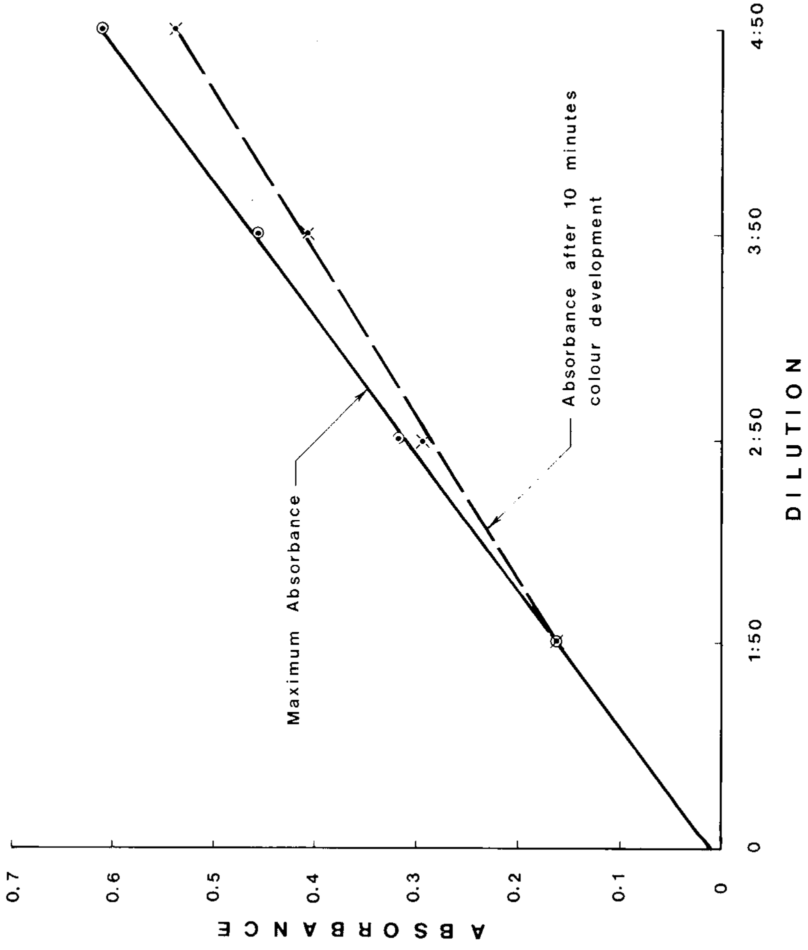

FIGURE 2 Absorbance versus dilution for sewage after digestion and colour development.

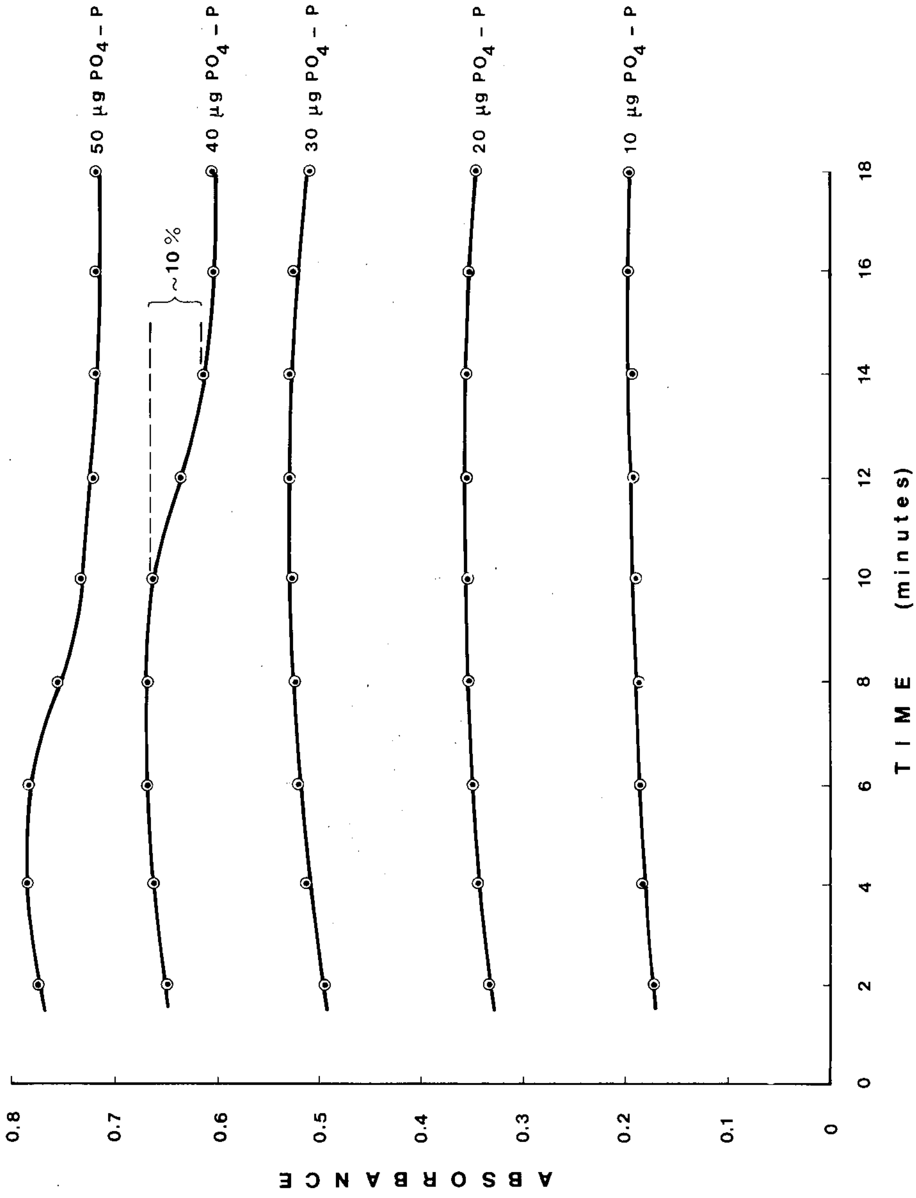

FIGURE 3 Colour development (absorbance versus time) for inorganic orthophosphate without digestion. Temperature 22 ±1°C.

quickly. With digested standards a reasonably stable maximum absorbance was obtained in the time interval 10–14 minutes for phosphorus levels up to 30 μg, corresponding to an absorbance of 0.5 units. The precision of analyses at higher phosphorus levels would necessarily be poorer due to changing colour and should be avoided. However, longer path-length cells could be used to advantage by restricting the phosphorus level to within the range where fading does not occur.

Salinity errors and interferences

The different colour development and fading behaviour observed during the analysis of different dilutions of sewage (Figure 1) indicates an interference. Nitrate nitrogen levels of up to 1 mg/l which were estimated to be present in some wastewater samples after dilution and digestion had no effect on the colour development and fading behaviour of standards. However, sodium chloride, at levels similar to those expected with diluted samples, had a marked effect. The results shown in Figure 4 for 20 μg phosphorus indicate a substantial interference, both in the lowering of the maximum absorbance obtained and in the time taken to reach the maximum. Salinity also causes the colour to fade more quickly, i.e. the maximum absorbance persists for a shorter period of time. Above 500 mg/l sodium chloride, however, the colour development and fading behaviour as well as the absorbance maxima are essentially the same.

Wooster and Rakestraw[9] found the opposite effect, i.e. the colour was more stable in saline solutions than in distilled water, but this may have been due to different concentrations of phosphate and reagents used in their study.

A graph of absorbance, both maximum and after 10 minutes for colour development, as a function of salinity for 20 μg phosphorus is shown in Figure 5. Above 500 mg/l sodium chloride, the absorbance readings after 10 minutes are 20% lower than that obtained for the same phosphorus level in distilled water after the same time interval. Analyses of samples, even with low salinities, will give low results when standard solutions in distilled water are used for comparison. This is due to salinity affecting both the maximum absorbance and the rate at which it fades.

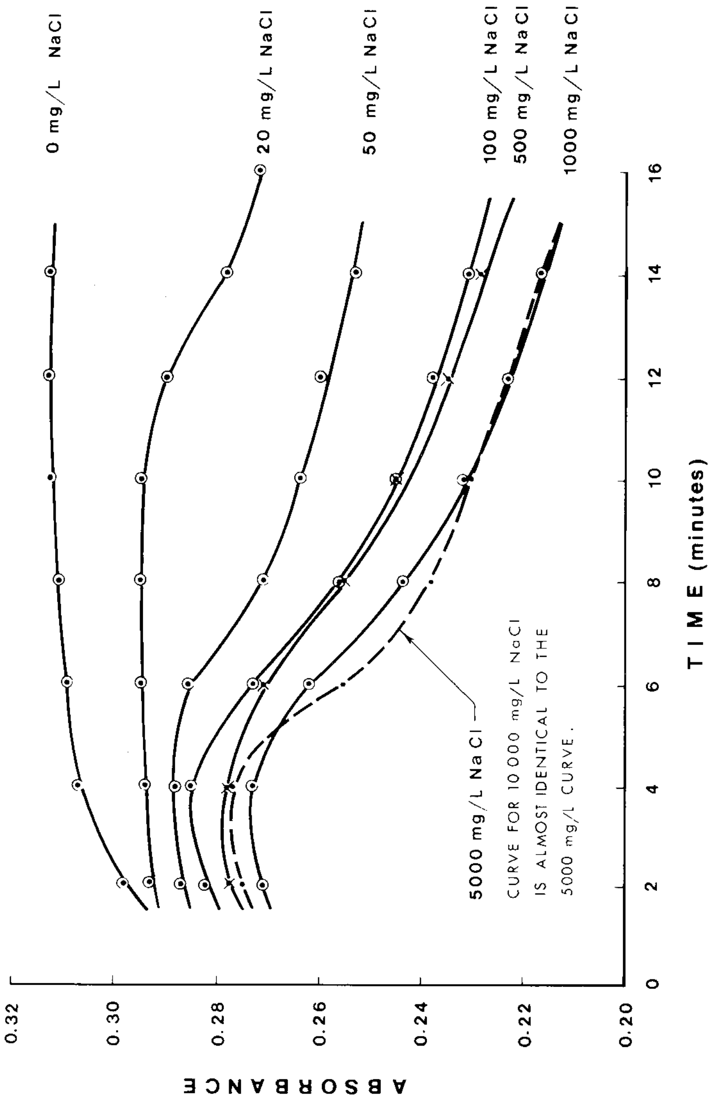

FIGURE 4 Colour development (absorbance versus time) for 20 μg inorganic orthophosphate with digestion and with varying levels of sodium chloride. Temperature 23 ± 1°C.

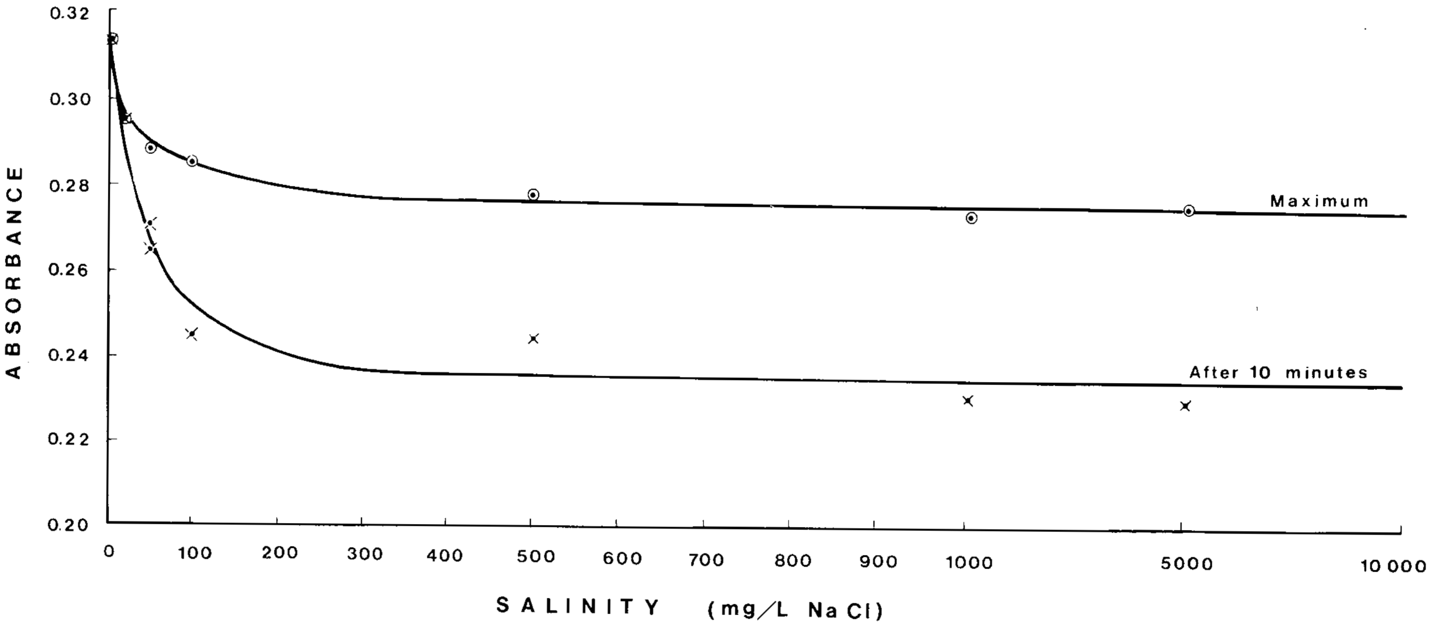

FIGURE 5 Absorbance after colour development for 20 μg orthophosphate as a function of salinity. Temperature 23 ± 1°C.

The phosphorus level itself was again found to affect colour development and fading behaviour but in a more marked manner. This is shown in Figure 6 for a salinity of 2,000 mg/l sodium chloride. A stable absorbance maximum is now obtained in the time interval 2–3 minutes for phosphorus levels up to 40 μg, and the calibration curve so obtained is linear.

The faster colour development and faster fading which occurs with increasing phosphorus concentration will also lead to the calculation of erroneously high levels of phosphorus if a standard addition technique is used and absorbance readings are made after 10 minutes. The use of absorbance maxima, i.e. after 2–3 minutes, will lead to correct results.

The behaviour demonstrated in Figure 1 for varying dilutions of sewage is a combination of salinity effects and effects due to varying phosphorus levels.

Since in the salinity range 500–10,000 mg/l the maximum colour is obtained in 2–3 minutes, addition of sodium chloride to both samples and standards to produce a salinity in this range and reading absorbances in this interval should eliminate errors. This was demonstrated by analysing sewage spiked with phosphate, with both samples and standards containing 2,000 mg/l sodium chloride (obtained by the addition of 10 ml of a 10,000 mg/l sodium chloride solution before digestion). For sewage a phosphorus level of 8.9 ± 0.1 mg/l (average of 5 replicates) was obtained. Another aliquot spiked with 10 mg/l phosphorus (using potassium dihydrogen phosphate) yielded a phosphorus level of 18.7 ± 0.2 mg/l by the same procedure, indicating a recovery of $98 \pm 3\%$, and thus overcoming errors associated with the original procedure.

Effect of temperature on colour development

The colour development behaviour of various phosphorus levels at 20° and 30°C after digestion and in the presence of 2,000 mg/l sodium chloride was investigated (Figure 7). In all cases an increase in temperature leads to an increase in maximum absorbance and causes the colour to fade more quickly. The magnitude of this temperature effect on the absorbance maxima is approximately 7% over the temperature range 20°–30°C, i.e. 0.7%/°C.

Samples and standards should therefore be of the same temper-

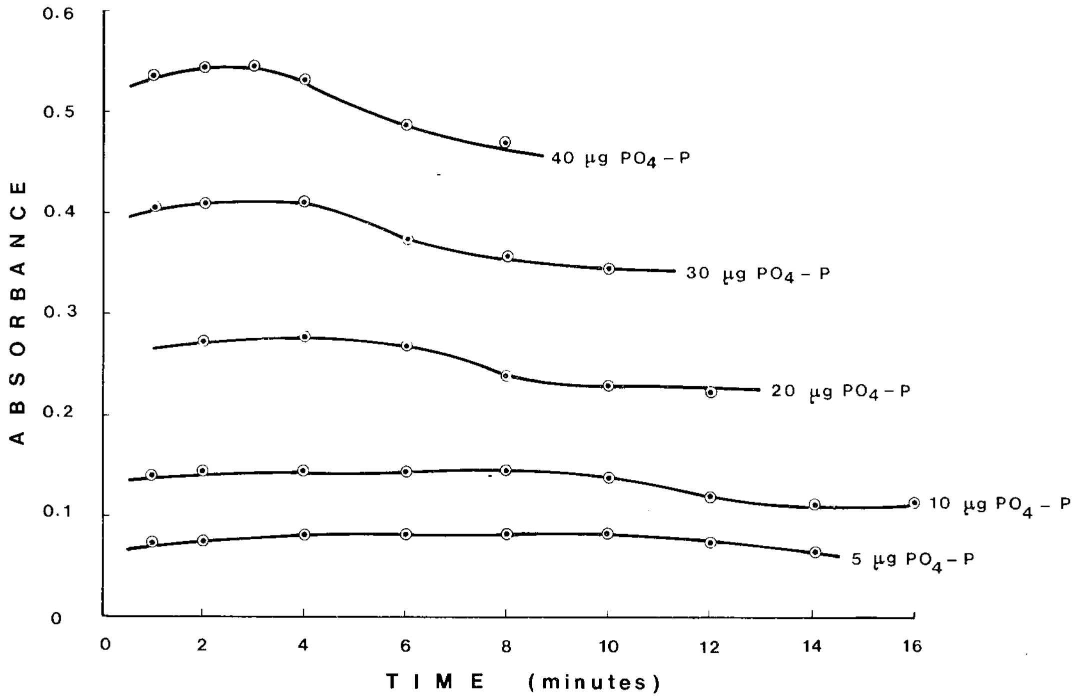

FIGURE 6 Colour development (absorbance versus time) for inorganic orthophosphate after digestion and in the presence of 2,000 mg/l sodium chloride. Temperature 24 ± 1°C.

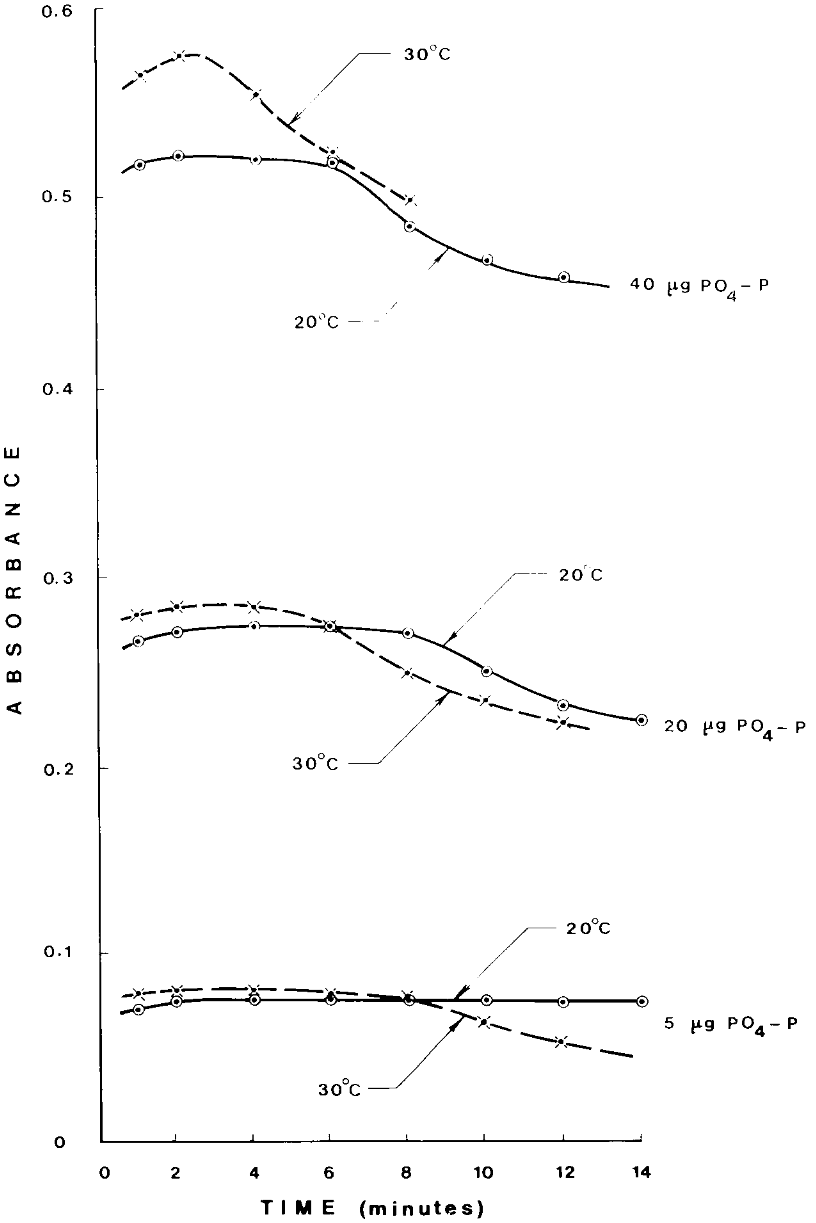

FIGURE 7 Colour development (absorbance versus time) for inorganic orthophosphate with digestion and in the presence of 2,000 mg/l sodium chloride at 20° and 30°C.

ature for maximum accuracy, but a small difference will have little effect. At temperatures between 20°C and 30°C the absorbance maxima are reached in the time interval 2–3 minutes for phosphorus levels up to 40 μg.

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