

Determination of phosphate at low concentrations in surface waters by flow-injection analysis

J J Pauer,^{1*} H R van Vliet¹ and J F van Staden²

¹ Hydrological Research Institute, Department of Water Affairs, Private Bag X313, Pretoria 0001, South Africa.

² Department of Chemistry, University of Pretoria, Pretoria 0002, South Africa.

Abstract

A flow-injection method for the determination of phosphate in surface waters was developed. The molybdenum blue colorimetric method with tin(II) chloride as reducing agent was used. The calibration curve was linear up to $500 \mu\text{g} \cdot \ell^{-1}$ while a good precision and accuracy were achieved. Using an Auto Analyzer colorimeter with a debubble type flow cell, a sample frequency of 90 samples $\cdot \text{h}^{-1}$ was obtained. To compensate for the interfering effect of mercury(II) on the sensitivity of the molybdenum blue reaction, both samples and standard solutions were preserved with the same amount of mercury(II) chloride.

Introduction

A variety of flow-injection methods are available for the determination of phosphate in water. Of these, flow-injection colorimetry is the best known and is currently most often used (Ruzicka and Stewart, 1975). Fogg and Bsebsu (1981; 1982; 1984) have also recently done work on flow-injection voltammetry. Colorimetric methods which have been adapted for flow-injection analysis (FIA) include the following:

- The malachite green method (Motomizu *et al.*, 1983) suitable for low level phosphate determination.
- The molybdovanadophosphoric acid method (Basson *et al.*, 1981) suitable for relatively high phosphate levels.
- The molybdenum blue method (Ruzicka and Stewart, 1975) which covers a wide range of phosphate concentrations.

The molybdenum blue method, based on the reaction between ortho-phosphate and molybdate in an acidic medium to form a molybdophosphoric acid, is the most commonly used. Selective reduction of the acid produces a substance with a blue colour.

A number of reducing agents have been recommended. Of these tin(II) chloride (Lutwak, 1953) and ascorbic acid (Murphy and Riley, 1962) are the most frequently used. In general ascorbic acid is preferable to tin(II) chloride, due to its higher stability and better precision (Strickland and Austin, 1959).

For low level phosphate determination, however, ascorbic acid reduction is too slow to provide adequate sensitivity (Janse *et al.*, 1983). The addition of antimony(III) as a catalyst accelerates the reduction rate, thus enhancing the sensitivity (Murphy and Riley, 1962). However, the sensitivity obtained with the latter method is still not sufficient to determine phosphate at concentrations below $1 \text{ mg} \cdot \ell^{-1}$. High antimony concentrations also lead to the formation of turbidity in the flow system with a concomitant decrease in the precision. Tin(II) chloride is more suitable for these determinations due to the faster reduction rate, which enhances sensitivity. The instability of tin(II) chloride has been overcome to a large extent by the addition of hydrazinium sulphate (Kolthoff, 1961).

This article describes a FIA method for the determination of phosphate in surface waters, using the molybdenum blue method. In view of the relatively low phosphate concentrations found in surface waters tin(II) chloride, stabilised with hydrazinium sulphate, was selected as the reducing agent.

Experimental

Apparatus

Sampler, peristaltic pump, colorimeter and recorder

A Technicon Auto Analyzer Sampler IV, with a modified sampling switching mechanism, was used to present samples to a Technicon Auto Analyzer model II peristaltic pump, fitted with standard Technicon pump tubes. A Technicon double channel colorimeter, with a 50,0 mm debubble type flow cell (internal diameter = 1,5 mm) was used. This was connected to a Technicon recorder.

Flow-injection valve system and timing device

A Carle valve (model 2014) with two variable sample loops was used to inject samples into the unsegmented carrier stream. The valve was driven by a Carle valve motor unit (model 4201) controlled by a locally constructed timing device, which switched both the valve and sampler units at the appropriate intervals.

Analytical flow system

A flow diagram of the analytical flow system is shown in Fig. 1. Polyethylene tubing (ID = 0,38 mm) was used for mixing coils and connecting tubes.

Optimisation of method

Sensitivity

To achieve optimum sensitivity, the effects of injection volume, coil length and reagent concentration were examined.

Fig. 2 shows the influence of the injection volume on the sensitivity. As could be expected the sensitivity increased with an increase in injection volume. The increase in the injection volume, however, caused greater carry-over between consecutive samples. An acceptable compromise between sensitivity and carry-over was found at $1\ 200 \mu\ell$, and this volume was used in further work.

Table 1 shows the influence of the length of the mixing coil (M) on the sensitivity. The difference in sensitivity between the 300 mm and 500 mm coil lengths was not significant. However, an improved flow pattern and less pulsation were obtained with the latter coil length which was consequently used.

*To whom all correspondence should be addressed.

Received 27 October 1987.

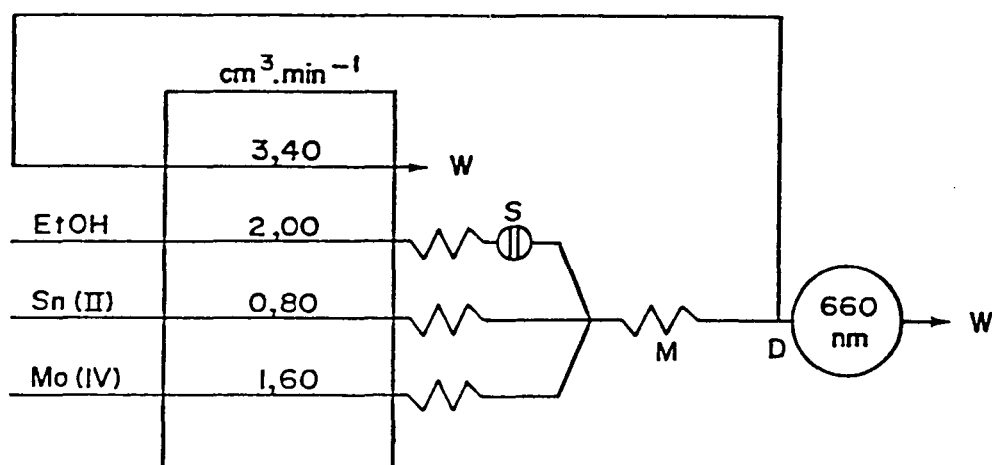


Figure 1
Schematic diagram of the analytical flow system. S = sampling valve;
D = debubbler; W = waste; M = mixing coil.

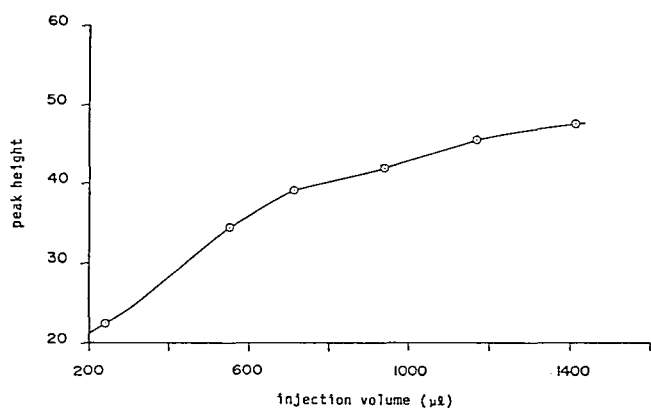


Figure 2
Influence of the injection volume on the sensitivity (in terms of peak height).

Sensitivity was also examined as a function of the reagent concentrations. The modified simplex method described by Deming and Morgan (1973) was used. Table 2 shows the range over which the reagent concentrations were investigated, as well as the optimum concentrations obtained. However, the stability of tin(II) chloride significantly influenced the precision of the method. Thus, while optimum sensitivity was found as a tin(II) chloride concentration of 0.32 g.l^{-1} , precision was poor. It was necessary to decrease the tin(II) chloride concentration to less than 0.1 g.l^{-1} to obtain acceptable precision.

Linearity

The linearity of the calibration curve was examined in a range from 0.05 to 0.50 mg.l^{-1} phosphate. The deviation from linearity with increasing phosphate concentration is shown in Fig. 3.

This is probably due to the lower tin(II) chloride concentrations being insufficient to fully reduce all of the molybdate in the molybdophosphoric acid. This led to the examination of the calibration curve as a function of tin(II) chloride concentration and injection volume. The results are shown in Fig. 4. A linear calibration curve was found at a tin(II) chloride concentration of 0.09 g.l^{-1} and an injection volume of $700 \mu\text{l}$.

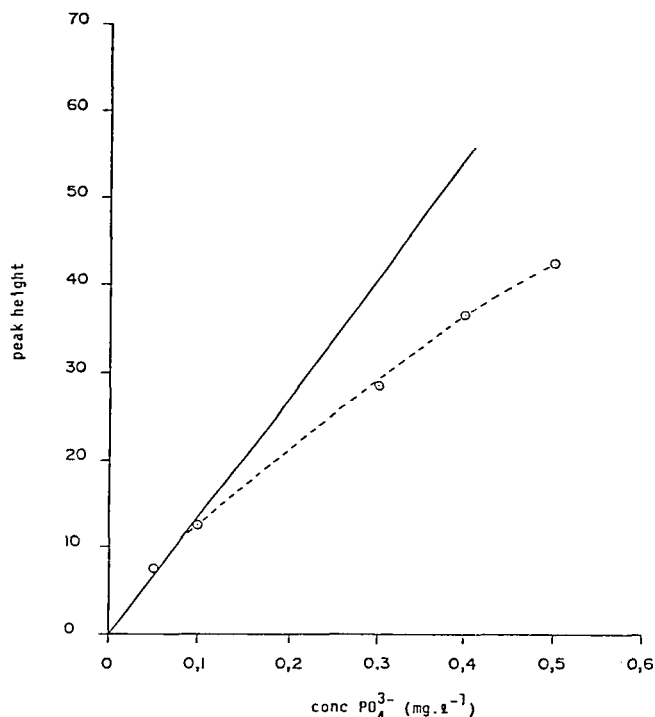
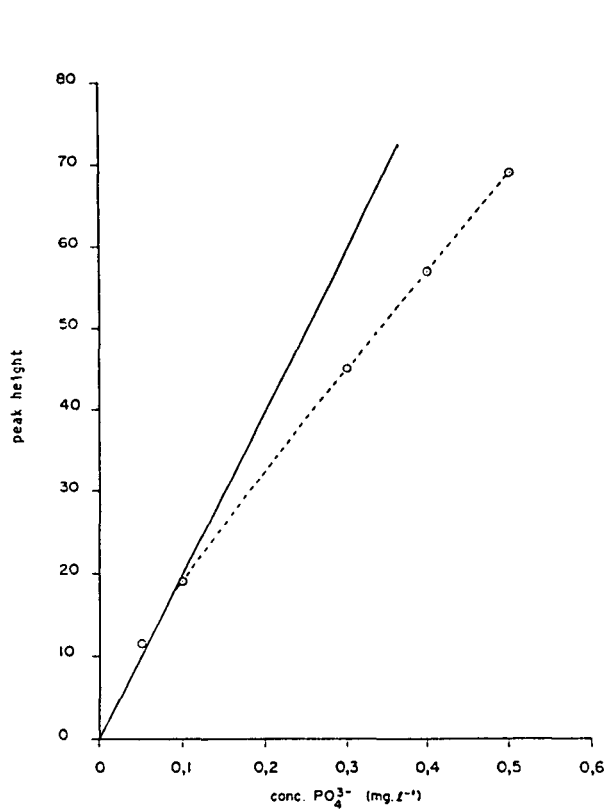
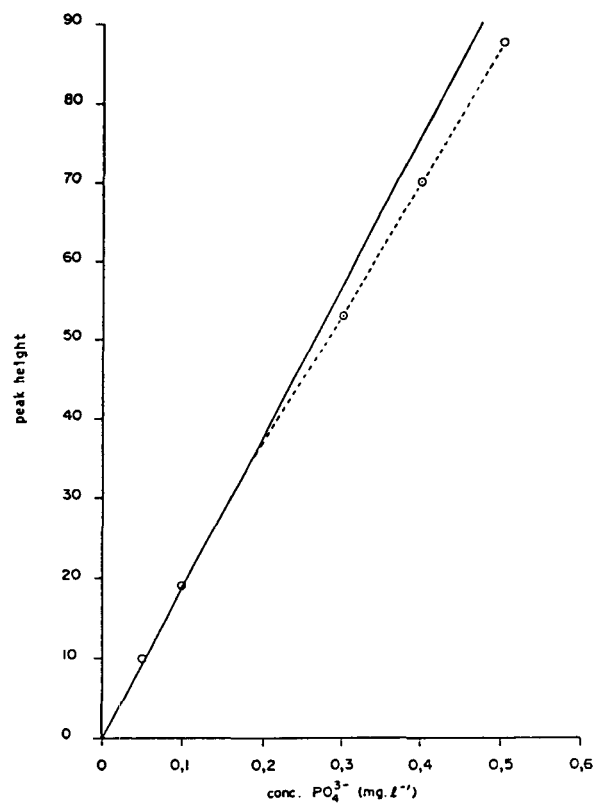


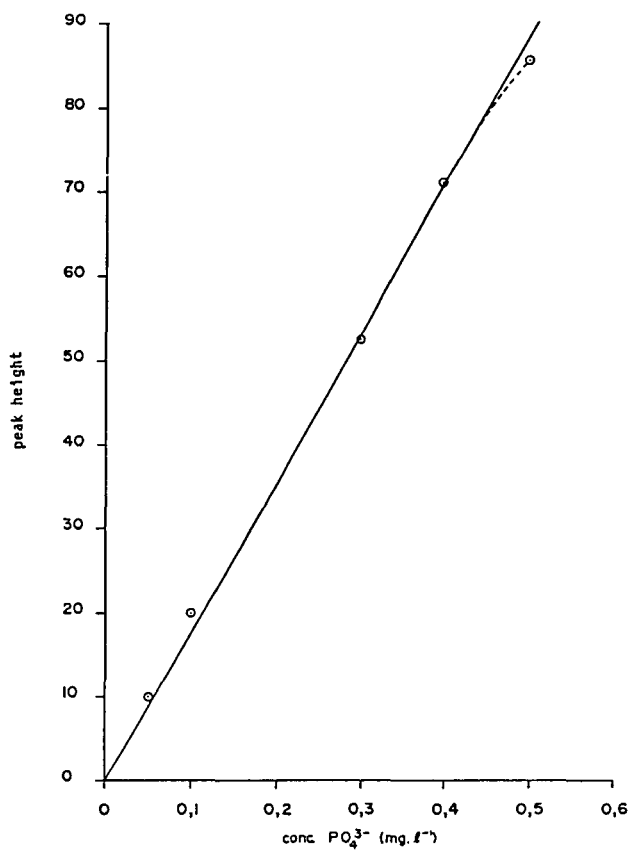
Figure 3
Linearity of the calibration curve.



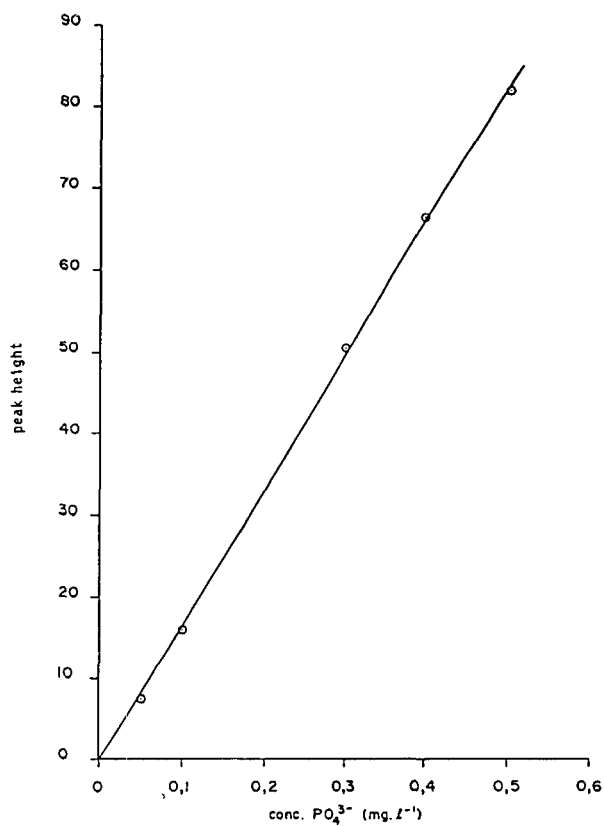
conc. tin $\text{Cl}_2 = 0.05 \text{ g.l}^{-1}$; injection volume = 1200 µl



conc. tin $\text{Cl}_2 = 0.09 \text{ g.l}^{-1}$; injection volume = 1200 µl



conc. tin $\text{Cl}_2 = 0.09 \text{ g.l}^{-1}$; injection volume = 900 µl



conc. tin $\text{Cl}_2 = 0.09 \text{ g.l}^{-1}$; injection volume = 700 µl

Figure 4
Linearity of the calibration curve as a function of tin(II) chloride concentration and injection volume.

TABLE 1
INFLUENCE OF THE COIL LENGTH ON THE SENSITIVITY (IN TERMS OF PEAK HEIGHT) OF THE METHOD.

Coil length (mm)	Relative peak height
0	65,0
300	73,4
500	73,5

TABLE 2
THE CONCENTRATION RANGES AND OPTIMUM CONCENTRATIONS OF THE REAGENTS USED IN THE MOLYBDENUM BLUE REACTION.

Reagent	Concentration range (g.l ⁻¹)	Optimum concentration (g.l ⁻¹)
Tin(II) chloride	0,20- 0,70	0,32
Hydrazinium sulphate	2,0 - 4,0	2,6
Ammonium heptamolybdate	2,0 -22,0	14,6

Recommended method

Preparation of the reagents

AR-grade reagents and deionised water were used throughout the experiment.

● Reducing agent:

Dissolve 0,09 g tin(II) chloride and 2,60 g hydrazinium sulphate in 1ℓ of a 0,5 mol.l⁻¹ sulphuric acid solution. Transfer the solution to an amber bottle and cover the bottle with plastic film.

● Molybdenum solution:

Dissolve 14,6 g of ammonium heptamolybdate-tetrahydrate in 1ℓ of a 0,63 mol.l⁻¹ sulphuric acid solution and add 2 ml sodium lauryl sulphate (SLS) solution. SLS solution is prepared by dissolving 15 g SLS in 85 ml of water.

● Ethanol solution:

Add 50 ml ethanol to a flask and dilute to 1 ℓ with water.

● Phosphate standards:

Weigh accurately 0,4390 g of sodium dihydrogen phosphate dried at 105°C for 2 h and dissolve in 1ℓ water. This stock solution contains 100 mg.l⁻¹ PO₄³⁻ - P. From the stock prepare 0,50; 0,40; 0,30; 0,10 and 0,05 mg.l⁻¹ P working phosphate standards. Both the stock solution and phosphate standards must be preserved with 20 mg.l⁻¹ mercury(II).

Evaluation of the method

All the water samples were preserved with 20 mg.l⁻¹ mercury(II) chloride throughout the investigation.

Accuracy

The accuracy of the method was determined by spiking four surface water samples. The results are shown in Table 3.

Precision

The precision of 16 repetitions of phosphate standard solutions in the range 0,05 to 0,50 mg.l⁻¹ PO₄³⁻ - P was determined. Table 4 summarises the data obtained in the evaluation of the precision of the recommended method. Fig. 5 is a recording chart illustrating three repetitions of the phosphate standard solutions in this range.

Interferences

Silica is the most important ion which interferes with the determination of phosphate in surface waters (APHA, 1985). The influence of silica on the method was examined. It was found that silica concentrations of less than 30 mg.l⁻¹ Si have no significant interference on the determination of phosphate using the recommended method.

Mercury(II) is frequently recommended as a preservative for phosphate in aqueous solutions (APHA, 1985). In a preliminary evaluation of the interfering effect of mercury(II) it was found that the presence of 7 mg.l⁻¹ Hg(II) (20 mg.l⁻¹ Hg(II)Cl₂) in both samples and standard solutions decreased the sensitivity of the reaction by approximately 5%. However, the addition of mercury(II) (7 mg.l⁻¹ Hg(II)) to both standard solutions and samples effectively compensated for the interfering effect of mercury. The validity of this approach is also supported by the satisfactory accuracy obtained with the recommended method.

Carry-over

Carry-over was determined by analysing a 0,50 mg.l⁻¹ standard followed by a 0,05 mg.l⁻¹ standard. At a sample frequency of 90 samples.h⁻¹ a carry-over of less than 1% was obtained.

TABLE 3
RECOVERY OF PHOSPHATE ADDED TO SURFACE WATER SAMPLES

Surface water sample	Phosphate (mg.l ⁻¹)		Recovery %
	Found	Expected	
1	0,34	0,35	97,1
2	0,28	0,28	100,0
3	0,48	0,47	102,1
4	0,49	0,50	98,0

TABLE 4
THE PRECISION OF CONCENTRATION READOUT GIVEN AS % RSD AT VARIOUS PHOSPHATE STANDARD SOLUTION VALUES.

Phosphate	Number of repetitions	% RSD
0,50	16	0,50
0,25	16	0,67
0,10	16	0,88
0,05	16	1,29

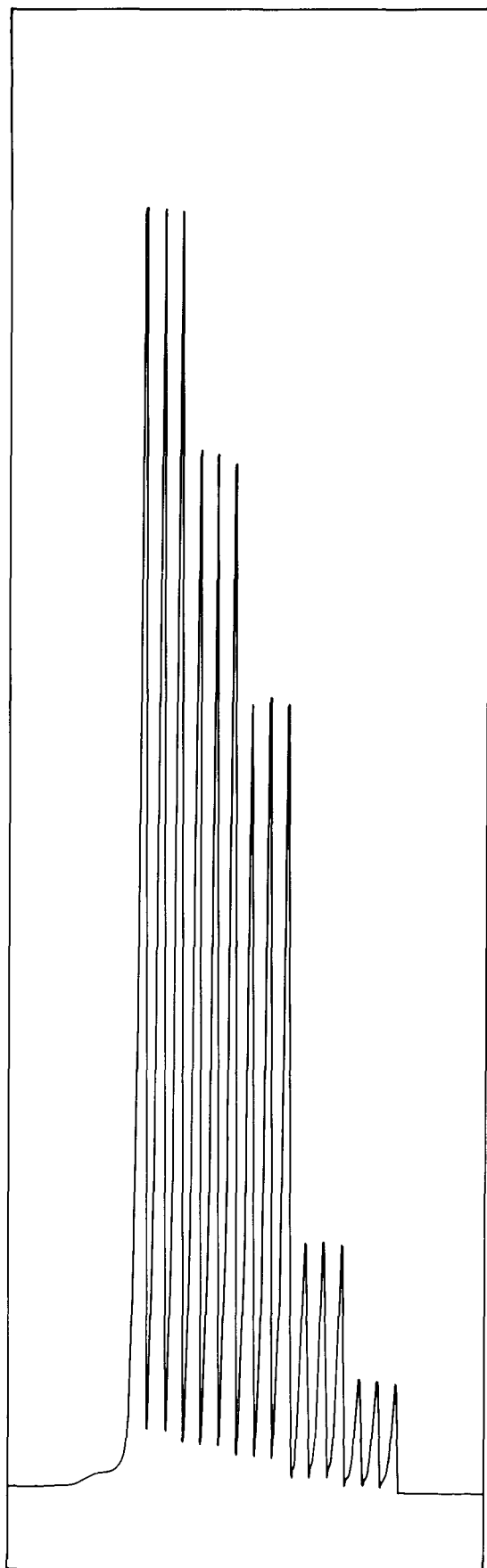


Figure 5
Recorder chart illustrating three repetitions of phosphate standard solutions in a range between 0,05 and 0,50 $\text{mg} \cdot \ell^{-1} \text{PO}_4^{3-} - \text{P}$.

Discussion

The recommended method has a suitable sensitivity to determine phosphate in a range between 0,01 and 0,50 $\text{mg} \cdot \ell^{-1} \text{PO}_4^{3-} - \text{P}$. A good precision (0,50% at 0,50 $\text{mg} \cdot \ell^{-1} \text{PO}_4^{3-} - \text{P}$) and acceptable accuracy was obtained. A carry-over of less than 1% was achieved at a sample frequency of 90 samples $\cdot \text{h}^{-1}$. The calibration curve is linear for the chosen concentration range.

The main disadvantage of using tin(II) as reducing agent is its low stability. Potentially this can lead to poor precision and a shift in the baseline. By reducing the concentration and adding hydrazinium sulphate, the tin(II) can, however, be stabilised. In addition, when the container holding the reducing agent is covered with plastic film, thus reducing exposure to atmospheric oxygen, the precision is improved and the baseline shift is almost eliminated.

The advantage of using a Technicon debubble type flow cell is that the occasional bubble is removed before reaching the detector. This is an advantage where the FIA method is used to analyse a large number of samples in a routine laboratory. The larger dead volume of this type of flow cell due to the debubble section and bigger tube diameter causes an increase in the dispersion of the samples. The greater dispersion increases the carry-over between consecutive samples, thus lowering the sample frequency. It is expected that the 90 samples $\cdot \text{h}^{-1}$ achieved with this flow cell can be considerably increased by replacing it with a narrow internal diameter FIA type flow cell.

Acknowledgements

The authors thank Mrs A Kolbe for drawing the figures and Mrs B Sutton for typing the manuscript. This paper is published with the permission of the Department of Water Affairs.

References

- APHA (1985) *Standard Methods for the Examination of Water and Wastewater* 16th Edition. American Public Health Association, Washington.
- BASSON, W.D., VAN STADEN, J.F. and CATTIN, P.M. (1981) Determination of phosphorus (P_2O_5) as molybdovanado-phosphoric acid in phosphate rock with a flow-injection procedure. *Fresenius Z. Anal. Chem.* **307** 373-377.
- DEMING, S.N. and MORGAN, S.L. (1973) Simplex optimization of variables in analytical chemistry. *Anal. Chem.* **45**(3) 278A-283A.
- FOGG, A.G. and BSEBSU, N.K. (1981) Differential-pulse voltammetric determination of phosphate as molybdovanado-phosphate at a glassy carbon electrode and assessment of eluants for the flow-injection voltammetric determination of phosphate, silicate, arsenate and germanate. *Analyst* **106** 1288-1295.
- FOGG, A.G. and BSEBSU, N.K. (1982) Flow-injection voltammetric determination of phosphate: Direct injection of phosphate into molybdate reagent. *Analyst* **107** 566-570.
- FOGG, A.G. and BSEBSU, N.K. (1984) Sequential flow-injection voltammetric determination of phosphate and nitrite by injection of reagents into a sample stream. *Analyst* **109** 19-21.
- JANSE, T.A.H.M., VAN DER WIEL, P.F.A. and KATEMAN, G. (1983) Experimental optimization procedures in the determination of phosphate by flow-injection analysis. *Anal. Chim. Acta* **155** 89-102.
- KOLTHOFF, I. (1961) *Treatise on analytical chemistry II. 3 Interscience*. New York.
- LUTWAK, H.K. (1953) The photometric determination of phosphorus in copper-based alloys containing tin. *Analyst* **78** 661-665.
- MOTOMIZU, S., WAKIMOTO, T. and TÔEI, K. (1983) Determination of trace amounts of phosphate in river water by flow-injection analysis. *Talanta* **30** (5) 333-338.

- MURPHY, J. and RILEY, J.P. (1962). A modified single solution method for the determination of phosphate in natural waters. *Anal. Chim. Acta.* 27 31-36.
- STRICKLAND, J.D.H. and AUSTIN, K.H. (1959) Refer to Murphy, J. and Riley, J.P. (1962). A modified single solution method for the determination of phosphate in natural waters. *Anal. Chim. Acta.* 27 31-36.
- RUZICKA, J. and STEWART, J.W.B. (1975) Flow-injection analysis, Part II: Ultrafast determination of phosphorus in plant material by continuous flow spectrophotometry. *Anal. Chim. Acta.* 79 79-91.
-