

Evaluation of a number of methods for the determination of trace amounts of phosphates with flow injection analysis (FIA)

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Abstract

Four different FIA/spectrophotometric analytical systems, namely tin(II) chloride (SnCl_2), ascorbic acid, malachite green and a rhodamine B methods, were optimised and evaluated in order to find the lowest detectable limit for each for the determination of trace amounts of phosphate on a routine basis. The SnCl_2 analytical system gave the best overall results. A low detection limit (2.5 $\mu\text{g/l}$) combined with a relatively large linear working range (1 to 400 $\mu\text{g/l}$) made this method superior to the others. The relatively unstable nature of SnCl_2 solutions together with blockages that occurred due to high concentration ranges are, however, factors to be considered when employing the method in routine laboratories.

Introduction

The nutritional needs of plants depend mainly on various concentrations of phosphates. A large number of commercially useful compounds contain phosphates in varying forms. Phosphates are added to boiler feed water to prevent scaling and are an essential constituent of fertilisers, of the body fluids, of soil and plants, and are also found in many industrial products from steels to detergents. The eutrophication of many natural waters has been attributed to the presence of appreciable concentrations of phosphate, so that many spectrophotometric determinations are performed to detect contamination or to control treatment of industrial effluent. Soluble orthophosphate and polyphosphates, in addition to organic-bound phosphates, may be found in water samples.

A variety of flow injection methods have been developed for the determination of phosphate in water. Of these methods, flow injection spectrophotometry is the best known and is currently most often used in various routine laboratories (Ruzicka and Hansen, 1975; 1988; Valcarcel and Luque de Castro, 1987; Ueno and Kina, 1983; Karlberg and Pacey, 1989; and Moeller, 1988). Flow injection voltammetry with voltammetric detection and reversed flow injection analysis also formed the basis of a procedure designed by Fogg and Bsebsu (1981; 1982; 1984).

The spectrophotometric determination of phosphate is based on the complexation of orthophosphate with acidic molybdate. The two main spectrophotometric methods available for phosphate determination are either the yellow coloured vanadomolybdate procedure for relatively high phosphate concentrations (Basson et al., 1981) or the molybdenum blue procedure for relatively low phosphate concentrations (Pauer et al., 1988). The molybdenum blue method, based on the reaction between orthophosphate and molybdate in an acidic medium to form a molybdophosphoric acid, is the most commonly used. Selective reduction of the molybdophosphoric acid produces a substance with a blue colour. Various reducing agents have been reported for the reduction of the phosphomolybdate complex to molybdenum blue, including hydrazine sulphate and sodium sulphite (Boltz, 1958);

hydroquinone, iron(II) sulphate and tin(II) chloride (Jackson, 1962); and ascorbic acid (Lacy, 1965).

In a developing country with limited water resources it is necessary to develop simple, economic methods to analyse pollutants on the μg level. The growth of living organisms in water can begin when orthophosphate concentrations reach a concentration of $6.5 \times 10^7 \text{ mol/l}$ (20 $\mu\text{g/l}$ P). It is, therefore, of utmost importance to be able to determine phosphate concentrations at this level. In the molybdenum blue procedure for relatively low phosphate concentrations the phosphomolybdate complex is reduced by either SnCl_2 or ascorbic acid to form a product which is detected. It is also possible to determine phosphate by complexing the phosphomolybdate-complex with malachite green or rhodamine B. The main objective of this study was to develop a method by which these low phosphate concentrations could be determined on a routine basis. Four flow injection analysis (FIA)-spectrophotometric methods for phosphate determination were optimised using univariate and simplex optimisation (Deming and Morgan, 1973; 1987; Moore, 1991; Moore and Bohmer, 1991; Massart et al., 1978; Malinowski and Howery, 1980; Massart et al., 1988; Meier and Zund, 1993).

Experimental

Four different FIA methods were optimised and evaluated; SnCl_2 , ascorbic acid, malachite green and a rhodamine B method.

Instrumentation

Flow system

Schematic diagrams of the different flow systems used, are outlined in Figs. 1, 2, 3 and 4. The manifolds consisted of Tygon tubing (inside dia. of 0.50 mm) cut into the required lengths and wound around glass tubes with an outside dia. of 10 mm. The following equipment also formed part of the FIA systems: Cenco and Gilson minipuls peristaltic pumps (operating at 10 r/min) were used to supply the different reagent streams and VICI 10 port multi-functional valves were used for injection of the samples. The valves, peristaltic pumps and the uv/vis detector were coupled to a computer. The whole FIA system in each procedure was controlled from the computer with a *FlowTEK* program (Marshall and Van Staden, 1992).

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