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FLOW INJECTION ANALYSIS OF INORGANIC ORTHO- AND POLYPHOSPHATES USING ASCORBIC ACID AS A REDUCTANT OF MOLYBDOPHOSPHATE

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A spectrophotometric method based on the formation of heteropoly blue complex was applied to the flow injection analysis of inorganic ortho- and polyphosphates such as diphosphate and triphosphate. Ascorbic acid was used to reduce molybdophosphate. Total amounts of inorganic ortho- and polyphosphates could be determined at a sampling rate of 45 samples/h with a relative standard deviation of less than 1%.

Flow injection analysis (FIA) is a simple and convenient approach to rapid chemical analysis by continuous flow.[1,2] In a previous paper[3] the present authors reported a high pressure flow injection system and its successful application to the rapid determination of inorganic ortho- and polyphosphates. An acidic molybdenum(V) and molybdenum(VI) mixed reagent was used to make possible the simultaneous achievement of both the hydrolysis of polyphosphates (P_n) and the color reaction of the resultant orthophosphate (P_1) according to Eq.1. This single reagent method was confirmed to be convenient and advantageous in such a FIA system.

$$P_n \xrightarrow{\text{Mo(V)-Mo(VI)}} (\ P_1\ ) \longrightarrow P_1\text{-Mo(V)-Mo(VI)} \qquad (\ 1\ )$$

On the other hand, there is another heteropoly blue method (Eq.2) that uses a couple of a molybdenum(VI) reagent and an ascorbic acid reagent.

$$P_n \longrightarrow (\ P_1\ ) \xrightarrow{\text{Mo(VI)}} P_1\text{-Mo(VI)} \xrightarrow{\text{Ascorbic acid}} P_1\text{-Mo(V)-Mo(VI)} \qquad (\ 2\ )$$

This "coupled reagent method" has already been applied to the air-segmented flow analysis of polyphosphates[4,5] and flow injection analysis of orthophosphate,[6,7,8] but has not yet been applied to the flow injection analysis of inorganic polyphosphates.

The purpose of this work was to examine the applicability of the coupled reagent method to the flow injection analysis of inorganic polyphosphates and to compare the efficiency of this method with that of the single reagent method.

Unless otherwise stated all chemicals used were guaranteed reagents.

A molybdenum(VI) reagent was composed of 0.04 M Mo(VI) (5.7×10^{-3} M, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) in 1.8 M H_2SO_4. A 0.05 M L-ascorbic acid solution containing 5% (V/V) acetone was used as a reducing agent. A molybdenum(V)-molybdenum(VI) reagent was prepared by partial reducing of molybdenum(VI) with sandy zinc in acidic solution,[3,9] and was composed of 0.02 M total molybdenum and ca. 1.9 M acid (H^+). Sample solutions of orthophosphate, diphosphate, and triphosphate were prepared by dissolution of potassium dihydrogen orthophosphate, KH_2PO_4, tetrasodium diphosphate decahydrate, $Na_4P_2O_7\cdot 10H_2O$, and pentasodium triphosphate hexahydrate, $Na_5P_3O_{10}\cdot 6H_2O$, respectively, in distilled water.

A schematic diagram of the flow injection system is shown in Fig. 1. The reagent solutions in reservoirs A and B were pumped out using a Kyowa KHU-W-52 reciprocating pump. A sample solution, ca. 50 µl, was introduced into the carrier reagent solution via a loop-valve injector (Seishin VMU-6). The introduced sample was then transported through the reaction tubing (RT, PTFE 0.5 mm ID, 1.5 mm OD, 10 m) to a detector. During this transport the sample, polyphosphate, is hydrolyzed to orthophosphate and the resultant orthophosphate reacts with reagents from reservoirs A and B to form a heteropoly blue complex. The absorption of this blue complex was monitored at 830 nm using a spectrophotometer (Hitachi 200-10) with a flow-through cell (volume 8 µl, path 8 mm). A narrow and long tubing (PT, PTFE 0.3 mm ID, 10 m) was applied at the exit of the flow-through cell, which gave the back pressure of 5 kg/cm^2 that was indicated on a pressure gage (Kyowa KPG 50N). Under such a high pressure the reaction tubing can be heated at 140 °C in a silicon oil bath (Thomas T-201) without the detector noise due to gas bubbling. A cooling tubing (CT, PTFE 0.5 mm ID, 1 m) was applied between the reaction tubing and the detector. An elastic pretubing (DT, Technicon Part No. 116 0528-01, 30 cm) was applied to dampen the pressure pulse caused by the reciprocating pump. A bypass tubing (BT, PTFE 0.3 mm ID, 1 m) was also applied to eliminate the injection shock.

Practical determination of inorganic ortho- and polyphosphates was carried out by two methods, i.e., the coupled reagent method and the single reagent method.

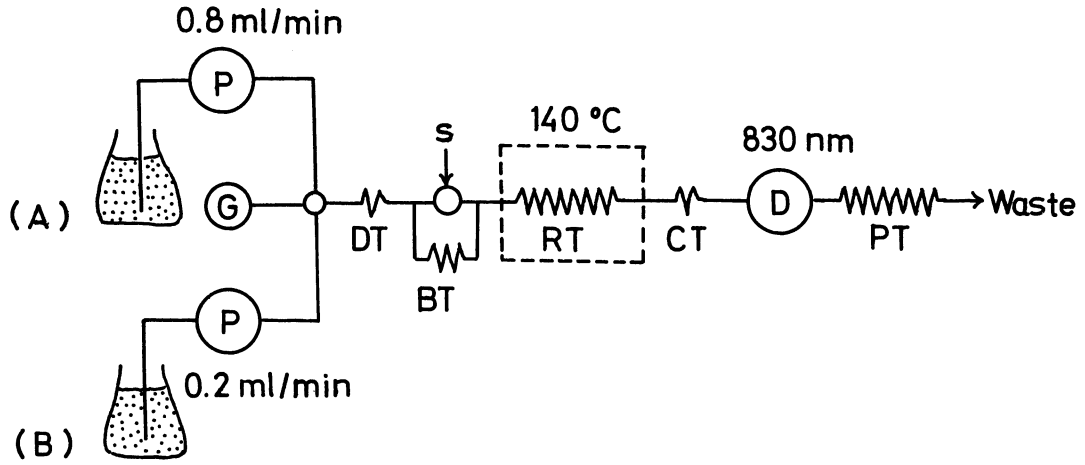

Fig. 1. Schematic diagram of the flow injection analysis of ortho- and polyphosphates. (A) and (B) ; reagent reservoirs, P ; reciprocating pump, G ; pressure gage, DT ; damper tubing, BT ; bypass tubing, S ; sample injection, RT ; reaction tubing, CT ; cooling tubing, D ; detector, PT ; back-pressure tubing.

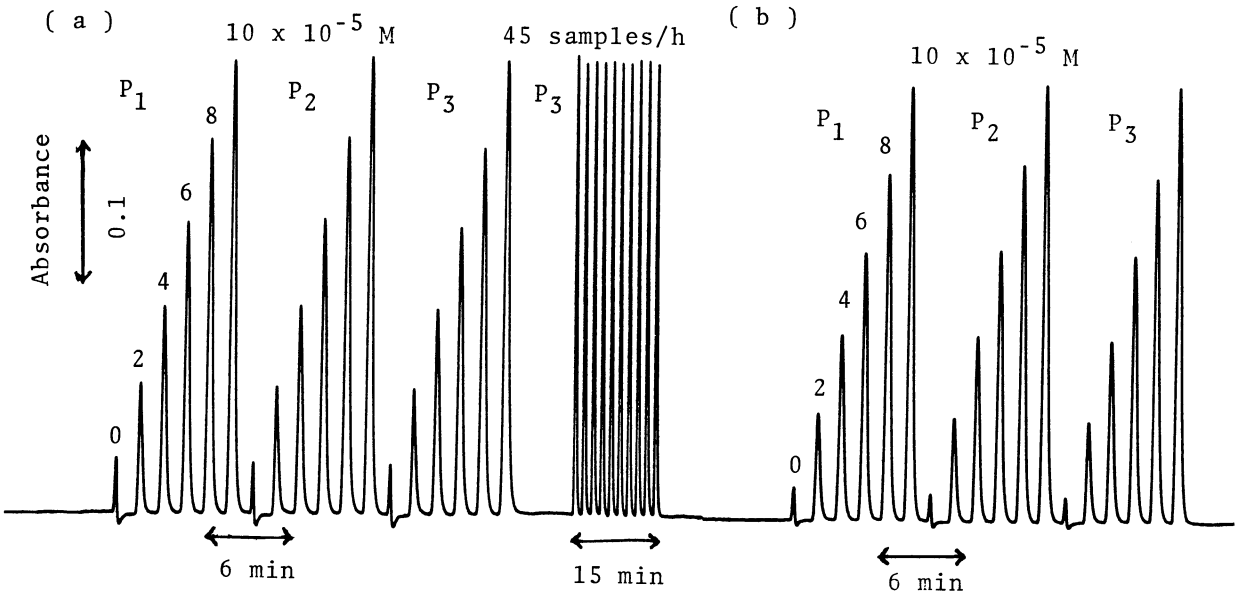

Fig. 2. Concentration profiles for orthophosphate (P_1), diphosphate (P_2) and triphosphate (P_3) obtained by the coupled reagent method (a) and by the single reagent method (b). The concentration of each sample increases from left to right, 0 - 10 x 10^{-5} M (as P). Ten times repetitive injections of triphosphate (10 x 10^{-5} M, as P) were also shown in (a) to demonstrate the reproducibility.

In the coupled reagent method, the molybdenum(VI) and the ascorbic acid reagents were separately filled in reservoirs A and B. In the single reagent method the molybdenum(V)-molybdenum(VI) reagent was filled in both reservoirs A and B.

Figure 2 shows the concentration profiles of orthophosphate, diphosphate, and triphosphate obtained by the coupled reagent method (a) and by the single reagent method (b). Each sample was injected successfully at the sampling rate of 45 samples/h. More than 98% (as P) of polyphosphates such as diphosphate and triphosphate were hydrolyzed and detected. Ten times repetitive injections shown for triphosphate by the coupled reagent method demonstrates good reproducibility (relative standard deviation < 1%), and the same reproducibility was also obtained by the single reagent method.

The peaks obtained even when solvent (water) was injected as a sample were assumed to be due not to the absorption, but to refraction.[10] The appearance of the "solvent peak" becomes very troublesome if one wants to detect polyphosphates at very low concentration. There is an attempt in our laboratory to eliminate the solvent peak and lower the limit of detection by modifying the design of manifold.

For the rapid determination of polyphosphates both the coupled reagent method and the single reagent method were concluded to be exellent and comparable with each other, with respect to the high sensitivity and good reproducibility. A minor difference is that the reagents for the coupled reagent method are less time-consuming to prepare, but one of them, the ascorbic acid solution, is less stable to store than the molybdenum(V)-molybdenum(VI) reagent.

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