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A New Preconcentration Method of Hydrophobic Substances in Water Using Polyvinylmethylether as a Thermo-responsive Polymer. Application to Spectrophotometric Determination of a Trace Amount of Phosphate in Natural Water

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A new method of concentration and separation for determining trace amounts of phosphate in natural water, using polyvinylmethylether(PVME), one of the thermally reverse polymers, was provided. When the solution was warmed to 45°C, PVME shrank greatly, so that the phosphomolybdate Malachit Green aggregate stuck to the walls along with PVME.

The preconcentration and separation are important for determination of trace substances in the environment such as river and sea water. A rapid and simple procedure is thus desirable.

In this paper, a new concentration procedure using polyvinylmethylether(PVME) is proposed for determining trace amounts of phosphate in water samples. PVME, a thermally reversible polymer,in aqueous solution exhibits a lower critical solution temperature(LCST) of ca.31°C. It is soluble in water below 31°C and shrinks abruptly to become insoluble on heating above 31°C. This feature is reversible with decrease or increase in temperature through LCST.[1,2] Collapse occurs due to phase transition of PVME at LCST. By the phase separation, certain hydrophobic substances in aqueous solution are incorporated into PVME through hydrophobic interactions between them in aqueous phase.[3] The phase separation of a thermally reversible polymer should thus be useful for selective extraction of hydrophobic substances in water.

Phosphate reacts with ammonium molybdate to form 12-molybdophosphate (P-MO), followed by ionic association with Malachite Green(MG) to produce a chromophore, P-Mo-MG aggregat{$(MG)_3Mo_{12}O_{40}$, denoted as P-Mo-MG} which is hydrophobic.[4] The P-Mo-MG aggregate was readily concentrated by PVME using only one test tube. The spectrophotometric determination of a trace amount of phosphate in water samples was successfully conducted.

Procedure for determination of phosphate : A sample solution containing phosphate(500 pmol to 20 nmol) was introduced into a 50 ml test tube provided with a stopper, followed by adding of 1 ml of 9 M sulfuric acid, 2 ml of Mo-MG reagent(mixture solution of 225 ml of 0.68 M ammonium molybdate and 190 ml of 2 mM MG and 36 ml of concentrated sulfuric acid) and 2 ml of 0.01% PVME, keeping the temperature of the solution below 25°C. When the mixture was warmed to 45 °C followed by shaking, the PVME gel shrank greatly, so that the P-Mo-MG aggregate along with PVME stuck to the walls of the test tube. The residual aqueous solution containing the remnant Mo-MG reagent was discarded by decantation. The P-Mo-MG aggregate was dissolved together with PVME in small volume(1— 2.5 ml) of methylcellosolve to measure absorbance at 627 nm. Phosphate was determined by the measurement of absorbance of the P-Mo-MG aggregate with PVME in methylcellosolve. When using the standard phosphate solution, absorbance gave a linear relationship in the range of 0.5 — 20 nmol phosphate. An apparent molar absorptivity of the P-Mo-MG aggregate was 2.6×10^{5} $M^{-1}cm^{-1}$. The method was successfully applied to the determination of phosphate in natural water samples such as tap water, mineral water and rainwater. Phosphate at part per billion levels in the sampls was determined in short time,30 samples being analysed within 60 min. Isolation of the phosphate aggregate with MG and its dissolution in a small volume of methylcellosolve are a simple, rapid and economical method using only one test tube to determine of phosphate in environmental water.

The mechanism for shrinking of PVME has so far not been clarified. However, it seems likely that phase separation takes place by association of the polymer molecules into larger aggregates formed by intermolecular hydrogen bonding and nonpolar bonds.[5)] The use of PVME provides a new means by solid phase extraction to separate hydrophobic substances from aqueous solution.

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