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Application of solidification of floating organic drop microextraction for inorganic anions: Determination of phosphate in water samples

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ABSTRACT

A novel dispersive liquid–liquid microextraction based on solidification of a floating organic drop (DLLME-SFO) for determination of orthophosphate was developed. The method includes the formation of molybdoantimonato-phosphoric heteropoly blue (HPB) followed by a DLLME-SFO procedure and subsequent absorbance measurement using a micro volume cell (5 μL) with 10 mm path length. The final experimental conditions for HPB extraction were found to be: 0.6 mL of ethanol as dispersive solvent containing 55 μL of 1-undecanol as extraction solvent, magnetic stirring at 500 rpm, 10 min extraction time, decreasing the stirring rate to 150 rpm in order to group all the droplets and then solidification of the organic droplet in an ice bath for 5 min under continuous magnetic stirring. It should be pointed out that no centrifugation step is required. The calibration plot was linear in the range 4.0–60 × 10^{-8} mol L^{-1} of phosphate, with a correlation coefficient of 0.9982. The limit of detection (LOD), calculated as three times the standard deviation of the blank test (n = 10), was 7.4 × 10^{-9} mol L^{-1} of phosphate. The reported procedure was applied for determination of phosphate in real water samples.

1. Introduction

With the constantly increasing social demand that new analytical methods meet the requirements of green analytical chemistry, we can observe several developments in different solvent-based microextraction procedures [1,2]. One of them is solidified floating organic drop microextraction (SFODME) [3]. Despite the intense development in this technique for determining both organic as well as inorganic analytes in recent years, we were unable to find any articles devoted to SFODME procedures for inorganic anions [4].

Phosphorus is an essential nutrient element determining biological productivity for aquatic environments [5,6]. Over-fertilization of agricultural land and subsequent runoff as well as the release from industrial or municipal sources has caused an excess of phosphorus input into natural waters, leading to eutrophication and consequently many other undesired effects, such as exponential growth of algal blooms and fish suffocation among others. The main and at the same time most bio-available fraction of phosphorus species in waters is represented by orthophosphate, commonly known as dissolved reactive phosphorus [7]. In surface waters, biological uptake through photosynthesis depletes phosphate concentration well below micromolar levels [8].

The most commonly applied technique for determination of orthophosphate is spectrophotometry, a determination that includes the formation of a yellow or blue (reduced) form of the heteropoly complex having the Keggin structure. The color can be enhanced by the formation of a mixed vanadomolybdate phosphate complex, by reduction with various reducing agents, or by formation of ion association complexes with basic dyes [7,9,10]. The modified ascorbic acid method of Murphy and Riley [11] with the addition of antimonyl tartrate is said to offer many advantages over methods using other reducing agents, such as tin(II) chloride or only ascorbic acid, for example a rapid reaction at ambient temperature, a stable product and less sensitivity to interference.

The extraction is recognized as a reliable method for the separation and determination of trace quantities of a number of elements in various materials. Procedures using the extraction of phosphate ion-associates with basic dyes are sensitive but often troublesome because the co-extraction of dye reagent gives rise to high absorbance of the blank test and worse repeatability [12]. Alcohols and ketones have the strongest extracting power among other oxygen-containing solvents. To the best of our knowledge, the extraction of heteropolymolybdate blue with higher alcohols has not previously been studied.

The aim of this work was to develop the SFODME procedure for determination of inorganic anion-phosphate in water samples. To the best of our knowledge, this is the first attempt at applying SFODME for determination of an inorganic anion. The method is based on the formation of heteropoly blue (HPB) followed by the DLLME-SFO procedure and subsequent spectrophotometric quantification. The developed

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procedure was applied for the determination of phosphate in real water samples.

2. Experimental

2.1. Chemicals and reagents

Unless stated otherwise, all the chemicals and solvents used were of analytical grade. Double-distilled water was used throughout the work. The glassware was cleaned by soaking in a phosphate-free detergent, acid washing and rinsing with water. The extraction solvents used (1-decanol and 1-undecanol) were purchased from Sigma-Aldrich (Slovakia). The dispersive solvents used (methanol, ethanol and acetone) were supplied by Centralchem (Slovakia). The sulfuric acid, potassium dihydrogenphosphate KH_2PO_4, ammonium molybdate tetrahydrate $(NH_4)_6Mo_7O_{24} \times 4H_2O$, and ascorbic acid (pharm.) used were from Centralchem (Slovakia), and the potassium antimonyl tartrate $K_2Sb_2(C_4H_2O_6)_2 \times 3H_2O$ from Sigma-Aldrich (Slovakia). The $(NH_4)_6Mo_7O_{24} \times 4H_2O$ was recrystallized from a water–ethanol solution prior to use, and the other chemicals were used as obtained without any additional purification.

A 0.01 mol L^{-1} stock solution of phosphate was prepared by dissolving 0.136 g of KH_2PO_4 in 100 mL of water. Phosphate working solutions in the range 1×10^{-6} to 1×10^{-5} mol L^{-1} were prepared daily by stepwise dilution of the stock solution. The 0.1 mol L^{-1} solution of $(NH_4)_6Mo_7O_{24} \times 4H_2O$, and 0.03 mol L^{-1} solution of $K_2Sb_2(C_4H_2O_6)_2 \times 3H_2O$ were prepared by dissolution of respective amounts of these chemicals in water. The mixed reagent contained sulfuric acid (6.6 mol L^{-1}), ammonium molybdate tetrahydrate (0.018 mol L^{-1}) and potassium antimonyl tartrate (0.003 mol L^{-1}) [13]. The solution was stored in an amber colored glass flask in a refrigerator at 4 °C. Ascorbic acid (0.5 mol L^{-1}) in water was used as the reducing solution.

2.2. Apparatus

A Lightwave II UV–Vis spectrophotometer (Biochrom, UK) with microvolume cells (Starna Scientific Ltd., England) of path length 10 mm (5.0 μL) was used for absorbance measurements. A magnetic stirrer model RH digital (IKA®-Werke GmbH & Co. KG, Germany) and a 28 × 7 mm stirring bar were used to stir the solutions. A UCI-150 ultrasonic cleaning bath (RAYPA, Spain) equipped with a high frequency generator (325 W power and 35 kHz frequency) was used as a source of ultrasonic energy. A VM-3000MD vortex mixer (Medline Scientific, UK) was used to assist the extraction process. Centrifugation was performed using a CN-2060 centrifuge (MRC, Israel).

2.3. Sampling and sample pre-treatment

Tap water samples were taken directly from our laboratory and analyzed using the reported method immediately after collection. River water samples were collected from the eastern region of Slovakia in February 2015 into bottles rinsed several times with the water to be analyzed and afterwards filled until overflow to prevent the effect of the oxygen in the headspace. The water samples were filtered through a 0.45 μm Millipore filter prior to the extraction to remove suspended particulate matter and stored in a refrigerator at 4 °C.

2.4. Extraction procedures

2.4.1. Conventional SFODME

A 10 mL volume of the phosphate working solution (1×10^{-6} mol L^{-1}) was placed into a 25 mL volumetric flask and then 0.5 mL of mixed reagent and 0.5 mL of a 0.5 mol L^{-1} solution of ascorbic acid were added. The volume was filled with water up to 25 mL and the solution was thoroughly mixed. The final concentration of phosphate in this solution was 4×10^{-7} mol L^{-1}. The solution was left to stand for 3 min for the formation of heteropoly blue.

Afterwards, all of the obtained HPB solution containing 1×10^{-8} mol of phosphate was transferred to a 50 mL beaker containing a stir bar (28 × 7 mm) and placed on a magnetic stirrer, and the magnetic stirrer was turned on. Next, 1.3 mL of concentrated sulfuric acid was safely added. Afterwards, a 90 μL volume of 1-undecanol was accurately placed onto the surface of the solution using a microsyringe, and the solution was stirred at 500 rpm at room temperature. Under these conditions, a vortex formed in the solution and the droplet remained in the top-center position of the aqueous sample. In this step, the analyte is extracted into organic phase. Afterwards, the sample vessel was transferred to an ice bath, where the organic solvent solidified within 5 min. The solidified solvent was then transferred using tweezers onto a watchglass, where it melted immediately. Finally, for the subsequent absorbance measurement the extract was transferred to a microvolume cell with 10 mm path length using an automatic pipette.

2.4.2. Vortex assisted SFODME

A 5 mL volume of the phosphate working solution (1×10^{-5} mol L^{-1}) was placed into a 25 mL volumetric flask. Then 0.5 mL of mixed reagent and 0.5 mL of a 0.5 mol L^{-1} solution of ascorbic acid were added. The volume was filled with water up to 25 mL and the solution thoroughly mixed. The final concentration of phosphate in this solution was 2×10^{-6} mol L^{-1}. Next, the solution was left to stand for 3 min for the formation of heteropoly blue.

A 5 mL volume of the obtained HPB solution containing 1×10^{-8} mol of phosphate was transferred to conical centrifugal tube, and 0.26 mL of concentrated sulfuric acid was safely added. Afterwards, a 90 μL volume of 1-undecanol was placed onto the surface of the solution using a microsyringe, and the solution was shaken using a vortex agitator at the highest possible speed (approx. 3000 rpm). In this step, a cloudy state formed, and the analyte was extracted into organic phase. The mixture was then centrifuged at 3000 rpm for 3 min. Afterwards, the sample vessel was put into an ice bath, where the organic solvent solidified within 5 min. The solidified solvent was then transferred using tweezers onto a watchglass, where it melted immediately. Finally, for subsequent absorbance measurement the extract was transferred to a microvolume cell with 10 mm path length using an automatic pipette.

2.4.3. Ultrasound assisted SFODME

A 5 mL volume of the phosphate working solution (1×10^{-5} mol L^{-1}) was placed into a 25 mL volumetric flask, and 0.5 mL of mixed reagent and 0.5 mL of a 0.5 mol L^{-1} solution of ascorbic acid were added. The volume was filled with water up to 25 mL and the solution thoroughly mixed. The final concentration of phosphate in this solution was 2×10^{-6} mol L^{-1}. Next, the solution was left to stand for 3 min for the formation of heteropoly blue.

A 5 mL volume of the obtained HPB solution containing 1×10^{-8} mol of phosphate was transferred to a conical centrifugal tube, and 0.26 mL of concentrated sulfuric acid was safely added. Afterwards, a 90 μL volume of 1-undecanol was placed onto the surface of the solution using a microsyringe, and the conical tube was sonicated at room temperature. In this step, a cloudy state formed, and the analyte was extracted into organic phase. The mixture was then centrifuged at 3000 rpm for 3 min. Afterwards, the sample vessel was put into an ice bath, where the organic solvent solidified within 5 min. Then, the solidified solvent was transferred using tweezers onto a watchglass, where it melted immediately. Finally, for subsequent absorbance measurement the extract was transferred to a microvolume cell with 10 mm path length using an automatic pipette.

2.4.4. Dispersive solvent assisted SFODME

A 10 mL volume of the phosphate working solution (1×10^{-6} mol L^{-1}) was placed into a 25 mL volumetric flask, and then