

CO-PRECIPIATION-ASSISTED COACERVATIVE EXTRACTION COUPLED TO HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY: AN APPROACH FOR DETERMINING ORGANOPHOSPHORUS COMPOUNDS IN WATER SAMPLES

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Organophosphorus (OPs) compounds are a large and diverse class of chemicals that have been synthesized for several purposes such as chemical weapons, flame retardants, ectoparasiticides and agrochemicals [1]. They are inhibitors of the acetylcholinesterase enzyme resulting in muscarinic and nicotinic symptoms and signs, even at low levels [1]. Drinking water is one of the main exposure routes to OPs for humans. There are current reports about water samples with OPs concentration up to 100 ng mL⁻¹ [2]. Do to their toxicity and potential risk for human health; it is required sensitive and selective analytical methodologies for analyzing OPs in water samples. The instrumental techniques generally reported for determination of OPs include high performance liquid chromatography (HPLC) with diode array detection as well as mass spectrometry and, to a lesser extent, gas chromatography with nitrogen-phosphorus electron capture and flame photometric detectors [3]. It is well known that the sample preparation step plays an important role in the analytical methodology for achieving the required analytical performance for determining OPs at trace levels. As alternative to traditional pre-treatment techniques, *e. g.*, liquid-liquid extraction or solid-phase extraction, green analytical techniques have been used for extraction and preconcentration of OPs. Coacervative extraction (CAE) technique is based on the use of ionic surfactants for extraction of analytes from aqueous samples [4]. Combination of CAE with co-precipitation agents that leads to a new analytical approach, named co-precipitation-assisted coacervative extraction (cop-CAE) technique [5], which has been recently investigated and applied in analytical chemistry. This technique is based on the formation of aggregated structures called “hemimicelles”, by mean of electrostatic interactions between monomers of ionic surfactant and complex species oppositely charged [5].

The aim of this work was to propose a cop-CAE technique for extraction and preconcentration of OPs in water samples after their HPLC analysis. The methodology was applied for determining five of the most used OPs in agriculture and indoor in Argentina

as target analytes: guthion, fenitrothion, parathion, methidathion and chlorpyrifos for their determination in tap and well water samples by HPLC-UV. The methodology was validated in terms of limits of detection (LODs), reproducibility, recovery (%) and linear working range and its fulfill US-EPA guidelines [6]. The developed methodology was applied for analyzing water samples from different locations of Mendoza.

EXPERIMENTAL

The studies and optimization assays lead to the following analytical methodology: 9 mL aliquot of water sample was added into a 15 mL centrifuge tube. Aliquots of 0.5 mL sodium citrate buffer 0.1 M pH 4, 0.08 mL aluminum sulfate 0.1 M and 0.7 mL sodium dodecyl sulfate (SDS) 0.1 M were then added to the tube and homogenized using a vortex stirrer (8 x g) for 8 min. The resulting cloudy solution was kept at 25 °C for 5 min before centrifuging at 1500 rpm (232 x g) for 10 min to accelerate the separation of phases. The resulting aqueous upper phase was removed and discarded while keeping the coacervate rich-phase for further analysis. A 700 µL aliquot of coacervate rich-phase obtained was dissolved with 300 µL of MeOH and stirred for homogenization. An aliquot of 20 µL the resulting solution was analyzed by HPLC-UV.

RESULTS AND DISCUSSION

Experimental variables that might condition the analytical responses of the OPs were evaluated on synthetic aqueous samples; including pH of solution, $\text{Al}_2(\text{SO}_4)_3$ and SDS concentration, stirring time, extraction temperature and time, and centrifugation. These studies were carried out by modifying one-variable-at-the-time while keeping the remaining constant. The chromatographic peak area was used to evaluate the impact of experimental conditions on the analytical signal of the target OPs.

Precursor of the co-precipitation agent and pH

Aluminum compounds were reported as precursor of the co-precipitation because of the aluminum species occurring within the pH range of 3.5 ~ 12.5 [7]. On the other hand, pH of the extraction media affects the electrostatic interactions between surfactant monomers and solid support. Based on these considerations, $\text{Al}_2(\text{SO}_4)_3$ was used as precursor of co-precipitation agent due to its pKa values (3.3-3.6). The assay of pH was carried out in the pH range 4-9; within which the targets OPs do not show degradation [8]. The fig. 1 shows that the highest relative response was achieved at pH 4. At this pH, the predominant aluminum specie is an hepta-charged aluminum complex, which is relevant for hemimicelles formation.

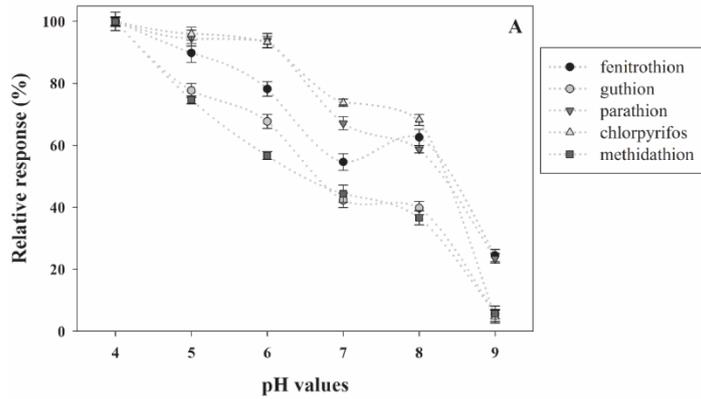


Fig. 1 Effects of pH on the relative response of OPs.

Al₂(SO₄)₃ and SDS concentration

Hemimicelles are formed at the “critical hemimicellar concentration” (HMC), leading to the coacervate-phase formation, which will be the extractant phase. Hemimicelles formation would be conditioned by the surface area of the hepta-charged aluminum complex, which depends on the Al₂(SO₄)₃ concentration. The highest relative responses of the target OPs was achieved at 0.8 mM Al₂(SO₄)₃ (fig. 2.A) and 7 mM SDS (fig. 2.B).

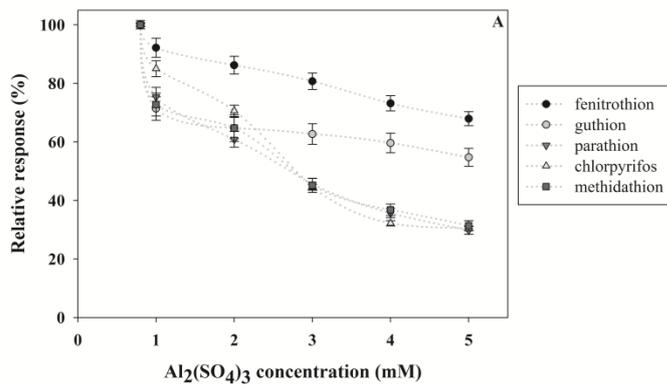
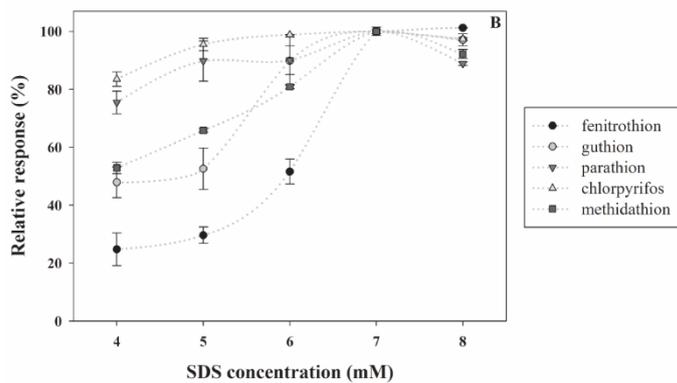


Fig 1. Effects of (A) Al₂(SO₄)₃ concentration on the relative response of OPs.



And (B) SDS concentration on the relative response of OPs.

Stirring time effect

Agitation of the solution during extraction process is essential to facilitate mass transference of the analytes from the matrix bulk to the hemimicellar phase, and to accelerate hemimicelles formation. The highest relative response for the target OPs was observed by stirring the solution with vortex for 8 min.

Analytical performance and application to real samples

Under optimum conditions, the proposed methodology exhibits successful performance in terms of linearity and precision, with recoveries and RSD values >81% and <8% respectively, and LODs within the range 1.1 – 2.5 ng mL⁻¹. The analytical figures of merits of the proposed methodology were comparable with other methodologies previously reported for determining OPs in water samples. Methidathion and chlorpyrifos were detected in well water samples from El Carrizal, at concentration levels of 10 and 7.5 ng mL⁻¹, respectively. This work represents a contribution about levels of OPs in environmental samples from Argentina.

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