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Solvent-assisted dispersive solid-phase extraction: A sample preparation method for trace detection of diazinon in urine and environmental water samples

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A B S T R A C T

In this research, a sample preparation method termed solvent-assisted dispersive solid-phase extraction (SA-DSPE) was applied. The used sample preparation method was based on the dispersion of the sorbent into the aqueous sample to maximize the interaction surface. In this approach, the dispersion of the sorbent at a very low milligram level was received by inserting a solution of the sorbent and disperser solvent into the aqueous sample. The cloudy solution created from the dispersion of the sorbent in the bulk aqueous sample. After pre-concentration of the diazinon, the cloudy solution was centrifuged and diazinon in the sediment phase dissolved in ethanol and determined by gas chromatography-flame ionization detector. Under the optimized conditions (pH of solution = 7.0, Sorbent: benzophenone, 2%, Disperser solvent: ethanol, 500 μL, Centrifuge: centrifuged at 4000 rpm for 3 min), the method detection limit for diazinon was 0.2, 0.3, 0.3 and 0.3 $\mu g\,L^{-1}$ for distilled water, lake water, waste water and urine sample, respectively. Furthermore, the pre-concentration factor was 363.8, 356.1, 360.7 and 353.38 in distilled water, waste water, lake water and urine sample, respectively. SA-DSPE was successfully used for trace monitoring of diazinon in urine, lake and waste water samples.

1. Introduction

O,O-diethyl *O*-(2-isopropyl-6-methylpyrimidin-4-yl) thiophosphate that known as diazinon is an organophosphorus insecticide with far-reaching non-agricultural and agricultural uses. Primary environmental concerns about using of this insecticide are pollution of surface water, bird kills and impacts on aquatic kinds. In many cases, diazinon and its metabolites have been monitored in various aquatic systems [1–3]. Besides, high quantity of diazinon residues have been monitored in urban waterways and sewerage [4,5]. Diazinon is a toxic insecticide according to the deterrence of acetylcholinesterase. The study of metabolites in animals have illustrated that the main path of metabolism is oxidation, and multiple metabolites with higher acetylcholinesterase deterrence activity have been recognized [6]. The usage of diazinon has been studied by many European environmental deputations in the past decade according to the major risk of its exposure with human health and environment. The indoor usage of diazinon is recently prevented by U.S. Environmental Protection Agency according to the important poisoning effect of diazinon on wildlife and humans [7]. As regards diazinon can also influence on the human nervous systems, concern about its use arises from the large amount applied and the production of rinse water from containers and application equipment. No drinking water standards exist for diazinon. The U.S. EPA has set a lifetime health advisory at 0.001 mg/L for diazinon in drinking water, however this health guidance level is not enforceable [8]. Different methods have been evaluated for the monitoring of diazinon using a diversity of techniques, including high-performance liquid chromatography, gas chromatography, immunoassay tests and mass spectroscopy [9–15]. According to the toxicity of diazinon, there is a need for acceptable, rapid, reliable, sensitive, and cost-effective sample preparation method for determining the presence of diazinon [16]. Thus, effective and reliable sample preparation methods such as solid-phase extraction (SPE), supercritical fluid extraction (SFE), pressurized liquid extraction (PLE), and solid-phase microextraction (SPME) have been of particular interest. However, some of these pretreatment methods need large amounts of sample and/or organic solvents, are time-

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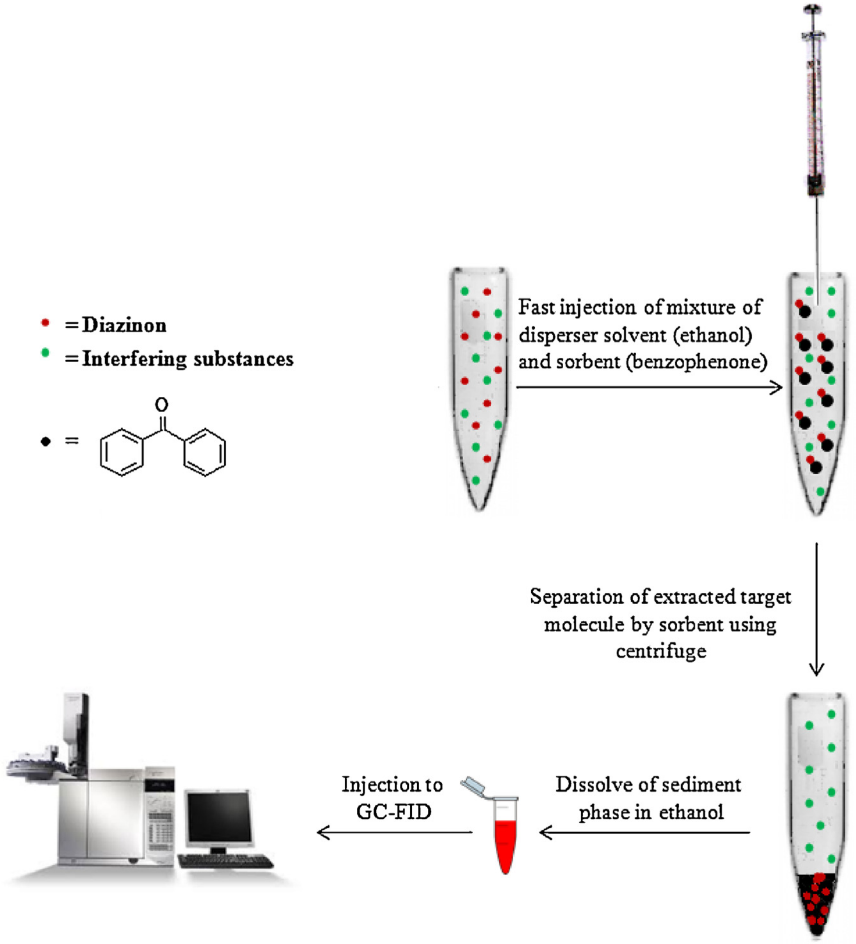

Fig 1. A scheme to present the extraction and monitoring of diazinon by the proposed sample preparation method.

Table 1
The figure of merits for analysis of diazinon in distilled water, waste water and lake water samples.

Sample	Regression equation	DLR[a] ($\mu g\,L^{-1}$)	MDL[b] ($\mu g\,L^{-1}$)	LOQ[c] ($\mu g\,L^{-1}$)	r^2	PF[d]
Distilled water	$Y = 9.46C\,(mg\,L^{-1}) + 0.383$	2-1000	0.2	2	0.99	363.8
Waste water	$Y = 9.26C\,(mg\,L^{-1}) + 0.434$	2-1000	0.3	2	0.99	356.1
Lake water	$Y = 9.38C\,(mg\,L^{-1}) + 0.481$	2-1000	0.3	2	0.99	360.7

[a] Dynamic linear range.
[b] Method detection limit.
[c] Limit of quantification.
[d] Pre-concentration factor.

Table 2
The figure of merits for analysis of diazinon in urine samples.

Sample	Regression equation	DLR[a] ($\mu g\,L^{-1}$)	MDL[b] ($\mu g\,L^{-1}$)	LOQ[c] ($\mu g\,L^{-1}$)	r^2	PF
Urine	$Y = 9.20C\,(mg\,L^{-1}) + 0.548$	2-1000	0.3	2	0.99	353.8

consuming and expensive, and have unsatisfactory enrichment factors. These problems could be addressed by the development of modular and compact processes that provide adequate separation and preconcentration without complex processes. SPE is more flexible and efficient than LLE in terms of simplicity, low consumption of the organic solvents, flexibility in choosing the adsorbent and high enrichment factor. Recently, SPE has been increasingly used for the preconcentration and separation of ultra-trace amounts of inorganic and organic species from complex matrices [17,18]. Solid-phase extraction techniques are surface-dependent processes since their efficiency directly depends on the particle size and the surface area of the sorbent [19]. Dispersive solid-phase extraction (DSPE) has risen as an alternative to conventional solid-phase extraction. It was, for the first time, proposed by Anastassiades et al. [20] and it can be considered as a quick, easy, cheap, effective, rugged, and safe (QuEChERS) sample treatment method. It is based on the SPE methodology, but the sorbent is added to the extract without conditioning, in small amounts (viz. 50 mg) and the dispersion is carried out assisted by an external energy (usually a vortex stirring). The phases are easily separated just by centrifugation. Sorbent dispersion leads to an increase of its active surface, and therefore to an improvement in the extraction kinetics. Moreover, this enhancement allows the use of a smaller amount of sorbent compared to the conventional extraction approaches resulting in the saving of mate-