

RAZVOJ I VALIDACIJA METODE ZA ODREĐIVANJE ODABRAHNIH ORGANOFOSFORNIH PESTICIDA U RAZLIČITIM VODENIM MATRIKSIMA PRIMENOM GC/MS TEHNIKE

DEVELOPMENT AND VALIDATION OF METHODS FOR DETERMINATION OF SELECTED ORGANOPHOSPHORUS PESTICIDES IN DIFFERENT AQUATIC MATRICES BY GC/MS

APSTRAKT

Organofosforne pesticidi (OPP) se relativno brzo razgrađuju te nemaju tendenciju bioakumulacije u životnoj sredini. Dodatno, niska tržišna cena uslovljava njihovu intenzivnu primenu. Stoga je u ovom radu razvijena i validovana metoda za određivanje šest jedinjenja iz grupe OPP u različitim vodenim matriksima primenom tačno-tečne ekstrakcije heksanom i gasne hromatografije sa masenom spektrometrijom. Određivanje efikasnosti ekstrakcije OPP ispitano je za tri vodena matriksa i to: sintetički (ultračista voda), sintetički matriks spajkovan različitim koncentracijama huminskih kiselina (HK) i prirodni matriks. Tačnost, izražena kao *recovery* određena je na dva koncentraciona nivoa i to za niži (2,4 µg/l) i viši (12 µg/l) opseg za sve vodene matrikse, dok je preciznost izražena kao relativna standardna devijacija (RSD) uzoraka u replikatu. Granica detekcije metode (MDL) za sva analizirana jedinjenja iznosila je od 0,039-0,155 µg/l. Tačnost i preciznost metode bila je u opsegu od 70-130% i 1,42-15%, redom, za sve ispitivane matrikse. Rezultati validacije metode pokazuju da je razvijeni metod pogodan za analizu OPP u različitim vodenim matriksima.

Ključne reči: organofosforne pesticidi, uticaj vodenog matriksa, validacija metode, GC/MS

ABSTRACT

Organophosphorus pesticides (OPPs) are a group of compounds which are relatively quickly degraded in the environment and have no tendency for bioaccumulation. Their low market price is a further reason for their intensive use. Therefore, the aim of this study was to develop and validate a method for the determination of six OPP compounds in various aqueous matrices using liquid-liquid extraction with hexane and gas chromatography-mass spectrometry. Determination of the efficiency of OPPs extraction was performed on three water matrices as follows: synthetic (ultrapure water), a synthetic matrix spiked with different concentrations of humic acid (HA) and natural water. Accuracy, expressed as recovery, was determined at two concentration levels (2.4 µg/l and 12 µg/l) for all of the water matrices, and the precision, expressed as relative standard deviation (RSD) of the replicate samples, was also calculated. Method detection limits (MDL) for all compounds analyzed ranged from 0.039 to 0.155 µg/l. The accuracy and precision of the method ranged from 70-130% and 1.42-15%, respectively, for all the matrices investigated. Validation results show that the developed method is suitable for the analysis of OPPs in various water matrices.

Key words: organophosphorus pesticides, water matrix impact, method validation, GC/MS

1. UVOD

Organofosforne pesticidi (OPP) su veoma popularne supstance koje se koriste u poljoprivredi širom sveta zbog svoje visoke efikasnosti u zaštiti useva. Po hemijskoj strukturi OPP su estri fosforne ili tiofosforne kiseline u kojima su vodonikovi atomi zamenjeni ugljeničnim komponentama, a atom fosfora okružen sa četiri atoma kiseonika (Akan i sar., 2015; Yan i sar., 2017). Međutim, široka primena i neadekvatno odlaganje OPP može da izazove ozbiljnu kontaminaciju hrane, životne sredine i svih ekosistema (Qian i Lin, 2015). Procena je da se godišnje primeni preko 4 miliona tona pesticida, pri čemu 1% od te količine bude

1. INTRODUCTION

Organophosphorus pesticides (OPPs) are very widely used substances in agriculture around the world, due to their high efficiency in crop protection. The OPPs are esters of phosphoric or thiophosphoric acids in which the hydrogen atoms are replaced with carbon components, and the phosphorus atom surrounded with four oxygen atoms (Akan et al., 2015; Yan et al., 2017). However, the widespread use and improper disposal of OPPs can cause serious contamination of food, the environment and the entire ecosystem (Qian and Lin, 2015). It has been estimated that more than 4 million tons of pesticides are applied annually, 1% of which is bio-accumulated

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