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Research Article

Gas kromatografi kütle spektrometresi ile sulama kanal suyu ve toprak numunesindeki fenazaquinin tayini

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Öz

Pestisitlerin tarımsal alanlarda gereğinden fazla ve yanlış kullanımlarının yol açtığı sağlık problemleri, pestisit kullanımının düzenlenmesi ve kontrol edilmesi için acil müdahalenin gerekliliğini doğurmuştur. Kontrolsüz pestisit kullanımının çevreye olan etkisi su ve toprak gibi çevresel kaynaklarda meydana gelen p ile kanıtlanmıştır. Fenazaquin tarım alanlarında yaygın olarak kullanılan ve canlı ve çevre sağlığı açısından olumsuz etki gösterdiği bilinen pestisitler içerisinde yer almaktadır. Bu çalışmada, iki farklı çevresel kaynaktan alınan numune analiz edilmiş; yüksek hassasiyete sahip bi gaz kromatografisi-kütle spektrometrisi (GC-MS) kullanılarak sulama kanal suyu ve toprak numunelerinde daha önce belirtilen pestisit 'fenazaquin'in tayini gerçekleştirilmiştir. Çalışmanın ilk aşamasında tespit limiti (LOD), tayin limiti (LOQ) ve bağıl standart sapma (RSD) değerleri sırasıyla 0.04 mg/L, 0.14 mg/L and 10.2% olarak belirlenmiştir.l Bir sonraki adımda, gerçek örnek matrislerinin analiz sonuçlarına etkilerini gözlemlemek amacıyla, yüksek konsantrasyonlu stok çözeltilerin düşük hacimleri ilave edilerek numuneler farklı kokonsantrasyonlarda hazırlanmıştır.Yapılan bütün ölçümlerde hassas analitik cihaz GCMS sisteminde geliştirilen uygun sıcaklık programı kullanılmıştır. Klasik geri kazanım prosedürünü kullanarak elde edilen sonuçlar yeterli derecede olmasına rağmen matris eşleştirme kalibrasyon stratejisinin kullanımı sayesinde geri kazanım oranı neredeyse %100'e yükseltilmiştir. Nitekim, bu çalışma iki farklı çevresel numunedeki fenazaquinin klasik geri kazanım ve matris eşleşme stratejisi ile tespit edilebileceğini açıklamaktadır. Sulama kanalı suyu ve toprak örnekleri tarım alanlarında kullanılan pestisitlerden kaynaklanan yüksek kontaminasyon riski altındadır.

Anahtar Kelimeler: Fenazaquin, Pestisitler; GC-MS

Determination of fenazaquin in irrigation canal water and soil samples by gas chromatography mass spectrometry

Abstract

The urgent call for the control and regulation of pesticide usage arose from the adverse health effects associated with their excessive and wrong application mostly in the agricultural field. The uncontrolled use of pesticides has been proved to affect the environment because of their ability to accumulate in different environmental resources such as water and soil. Fenazaquin is one of the mostly used pesticides in the agricultural field known by its adverse health effects. In this study, the previously mentioned pesticide "fenazaquin" was analyzed in two different kind of environmental samples: irrigation canal water and soil samples using a highly accurate gas chromatography mass spectrometer (GCMS). In the first step of the study, the limit of qualification (LOD), limit of quantification (LOQ), and relative standard deviation (RSD) were determined and calculated to be 0.04 mg/L, 0.14 mg/L and 10.2%, respectively. In the following step, the samples were spiked at different concentrations using low volumes of high concentration stock solution, to ensure the real effects of the sample matrices were observed. All measurement were performed by applying the adequate temperature program of the sensitive analytical instrument GCMS. The results obtained using the classical recovery procedure was satisfactory but matrix matching calibration strategy was used to improve the percent recoveries to almost 100%. Thus, this study explains the possibility of fenazaquin determination in two different environmental samples using the classical recovery and matrix matching strategies. Irrigation canal water and soil samples are on a high contamination risk from the pesticides used in the agricultural field.

Keywords: Fenazaquin; Pesticides; GC-MS

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1. Introduction

Pesticides are mainly used to control, prevent and eradicate pests from agricultural fields and households that usually pose a serious nuisance to human beings and other living organisms (Pan et al., 2019). Based on the target organism, pesticides can be classified as herbicides, insecticides, bactericides, fungicides, etc. (Kim, Kabir, & Jahan, 2017). Pesticides contain mainly natural extracts from plants and dozens of chemically synthesized compounds that are used to ameliorate the pesticide effectiveness and shelf-life (Bulgurcuoğlu, Yılmaz, Chormey, & Bakırdere, 2018). An increase in the worldwide consumption of pesticides has been reported in many diverse areas including agriculture, gardens, public places, hospitals and others (Ramakrishnan, Venkateswarlu, Sethunathan, & Megharaj, 2018). The inappropriate usage of pesticides and the application of high dosage may lead to harmful consequences that affect the health of living organisms and contaminate environmental resources such as water, air and soil (Jayaraj, Megha, & Sreedev, 2016). Exposure routes such as consumption of contaminated water or food and inhalation of polluted air, together with the type of pesticide and duration of exposure define the severity of the effects on human health and living organisms (Dhananjayan & Ravichandran, 2018). The respiratory, cardiovascular, reproductive, immune, endocrine and nervous systems are influenced mainly by the long period exposure to pesticide at low levels (Souza et al., 2011).

Fenazaquin (4-(2-(4-t-butylphenyl) ethoxy) quinazoline) is a member of the quinazoline group of pesticides that act by inhibiting the electron transfer of the mitochondrial respiratory chain (Sangeetha & Ramaraju, 2013). Fenazaquin acts against the phytophagus mites found mainly in agricultural staple foods such as almonds, grapes and citrus fruits (Solomon, Fitzgerald, & Ridout, 1993). The European Commission approved its use and limit the daily intake (ADI) to 0.005 mg/kg body weight/ day (Elanco, 1993).

Pesticide analysis is widely conducted by instrumental chromatography, mainly liquid chromatography (LC) and gas chromatography (GC). The selection of the suitable chromatographic instrumentation is based mainly on the physical characteristics of the mobile phase such as polarity, thermal stability and volatility (Coskun, 2016). It is reported that GC is more suitable for volatile compounds in comparison to LC which is applied to more polar and non-volatile compounds (Chormey, Karakuş, et al., 2017). GC can be coupled with different detection systems including thermal conductivity detector (TCD), electron capture detector (ECD), nitrogen phosphorus detector (NPD) and flame photometric detector (PID), flame ionization detector (FID) (Chormey, Büyükpınar, Turak, Komesli, & Bakırdere, 2017; Rahman, El-Aty, & Shim, 2015). A more sensitive, accurate and precise determination of compounds is achieved when GC is coupled with mass spectrometry (MS) (Lindon, Tranter, & Koppenaal, 2016). In addition to chromatographic separation based on different retention times, the mass spectrometer also separates compounds from each other based on different mass-to-charge ratio ions. This allows selective and specific determinations to be carried out for compounds (Bulgurcuoğlu et al., 2018; Kapukıran, Fırat, Chormey, Bakırdere, & Özdoğan, 2019). Complex sample matrices present interferences that affect the accuracy of quantifying analytes. These interferences could result in false negative or false positive results (Chormey Dotse et al., 2018).

This study was therefore aimed at determining fenazaquin in complex environmental samples and using matrix matching calibration method to offset interferences for accurate quantification.

2. Material and Methods

2.1. Apparatus

Fenazaquin was analyzed with a 6890 model Agilent (USA) gas chromatograph equipped with a non-polar HP-5MS column having film size value, internal diameter and length of 0.25 µm, 250 µm and 30 m, respectively. The identification and quantification of fenazaquin was achieved with a 5973 model Agilent mass spectrometer connected to the gas chromatographic system. The quantifier and qualifier ion were selected as 145 and 160 (m/z), respectively, and data acquisition was in the selected ion monitoring (SIM). Fenazaquin was eluted using a single temperature ramp program (40 °C/min) from an initial temperature of 70 °C to 280 °C and held for 2.35 min. The MS source, MS quad, Ms transfer line and the temperature of the injection port were fixed at 230 °C, 150 °C, 280 °C and 250 °C, respectively. Sample injection was performed in the splitless mode with a fixed volume of 1.0 µL for each analysis, and the flow rate of helium carrier gas was set constant at 1.4 mL per minute.

2.2. Chemicals and reagents

Fenazaquin ($C_{20}H_{22}N_2O$) standard (CAS# 120928-09-8) was purchased from Dr. Ehrenstorfer GmbH (Germany) with a percent purity of 99.0%. The stock solution of fenazaqouin was prepared in methanol and stored at -18 ºC for further use. Calibration standards and intermediate standard solutions were prepared by diluting the stock solution with deionized water which was obtained from an ELGA - VEOLIA Flex 3 ultra-pure water system. Analytical grade chemicals purchased from Merck - Germany were used in this study.

2.3. Samples

Soil samples were taken from different locations of the same university campus of Yildiz Technical University, Davutpasa campus. Soil samples were homogenized, grinded and sieved to obtain one bulk sample with very fine particles having sizes less than

0.10 cm. Water from an irrigation canal was sampled into plastic bottles after being rinsed adequately and stored under room conditions in a wooden cabinet. The water sample was filtered using 12 µm filter papers prior to each analysis.

3. Results and discussion

All measurements in the study including calibration standards and spiked samples were done in triplicates and the average values used for developing calibration plots and calculating percent recoveries.

3.1. Qualitative and quantitative determination of Fenazaquin

A standard solution of fenazaquin (20 mg/L) was eluted using the temperature program given in section 2.1. Fenazaquin was eluted at a retention time of 7.03 min as shown for the extract ion chromatogram of Figure 1 for the four most prominent ions. Standard solutions were prepared between 0.10 – 100 mg/L to develop a calibration plot which was linear between 0.20 and 50 mg/L, with a coefficient determination value (R^2) of 0.9993. The standard deviation (StdDev) value for six replicate measurements of the lowest calibration standard (0.20 mg/L) was used to calculate the limit of qualification, limit of quantification and percent standard deviation (%RSD) using the equations below:

LOD: 3 x StdDev/slope (1)
LOQ: 10 x StdDev/slope (2)
%RSD: (StdDev/Average) x 100 (3)

The values calculated for LOD, LOQ and %RSD were 0.04 mg/L, 0.14 mg/L and 10.2%, respectively. The linearity of the calibration plot can be seen in the calibration plot of Figure 2 (R^2=0.9993) and low %RSDs shows good instrumental repeatability.

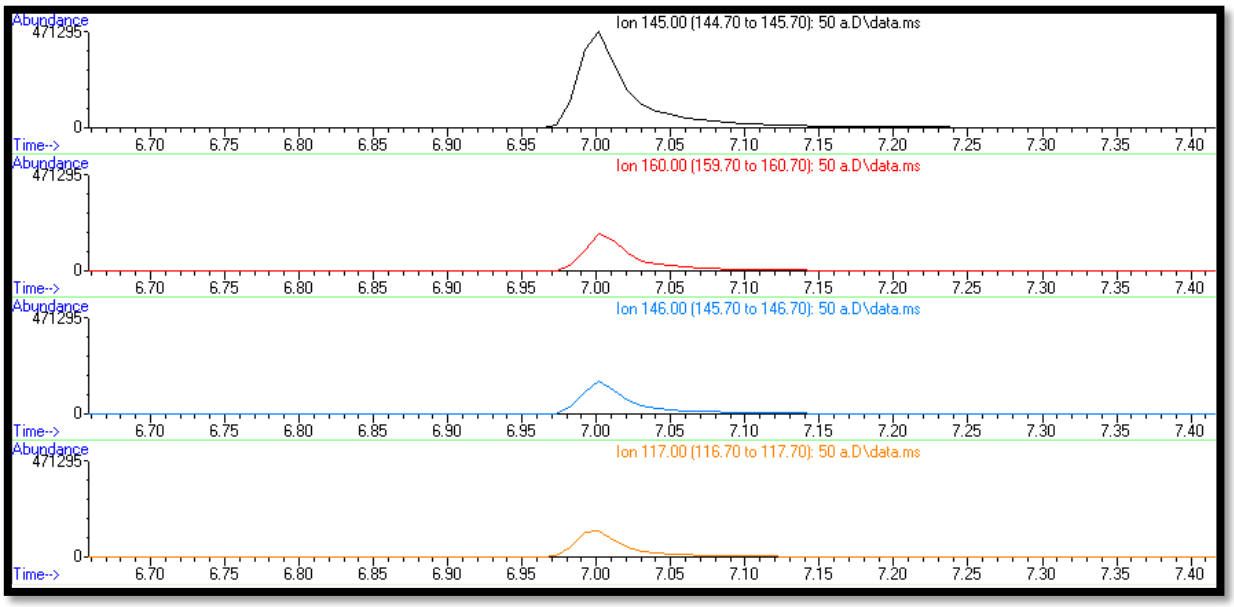

Figure 1. Extraction chromatogram for the four most prominent ions of fenazaquin.

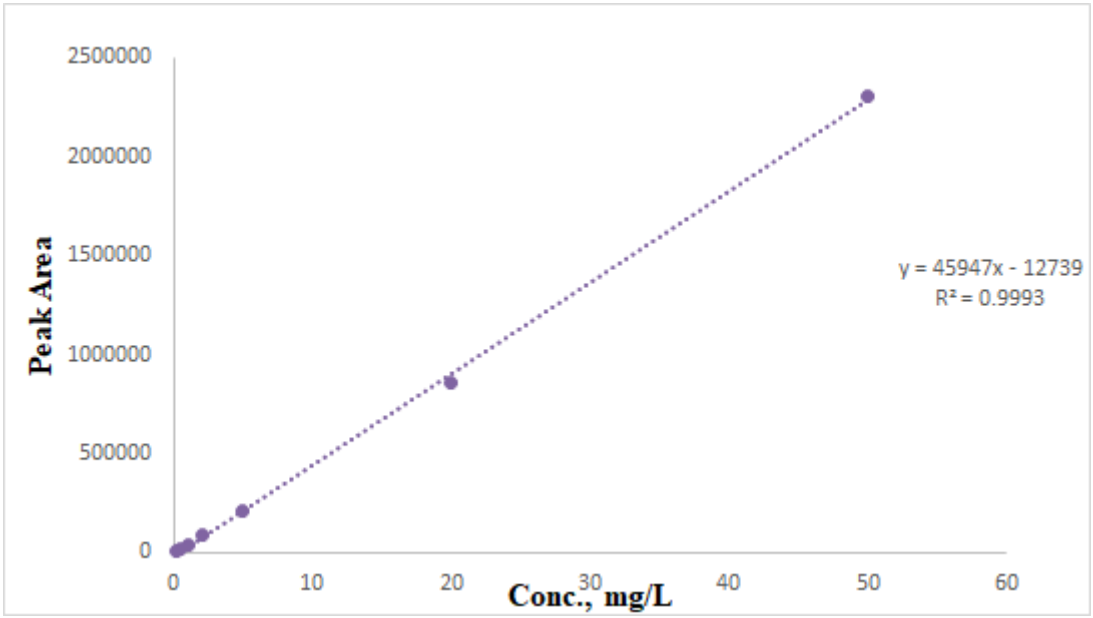

Figure 2. Calibration plot of fenazaquin standard solutions (0.20 – 50 mg/L).

3.2. Recovery studies in irrigation canal water

Irrigation canals are viable sources of water needed to ensure regular and timely irrigation of agricultural crops. Since these canals are not covered, they are prone to contamination during and after application of pesticides, and this may increase in quantity over. Water from an irrigation canal situated on a farmland was directly measured by the GC-MS system to determine whether or not fenazaquin was present. The blank analysis did not produce an analytical signal at the retention time of fenazaquin and was therefore considered to be clean. In order to evaluate the effect the irrigation canal would have on the analyte, spike recovery tests were performed at 2.0, 5.0, 10 and 50 mg/L. With respect to the calibration standards used in validating the GC-MS system, the percent recoveries for spiked irrigation canal samples fell below 80%. Thus, matrix matching was employed by preparing the calibration standards in a different irrigation canal matrix, which recorded an R^2 value of 1.000. The peak area values of the spiked samples were very close to their corresponding calibration standards and this produced 101.6 ± 3.6%, 99.2 ± 3.0%, 100.0 ± 7.5% and 100.1 ± 4.7%.

3.3. Recovery study in soil samples

The soil is one of the most easily contaminated resources after application of pesticides. The balance of the ecosystem stands great risk from such contaminations because of the potential adverse effects on non-target plants and microorganisms in the soil. Fine soil samples (0.50 g) were spiked with fenazaquin standard solution to final concentrations of 5.0, 10 and 20 mg/kg and allowed to dry completely for 2.0 h at 70 °C. Then, the soil samples were transferred into 15 mL centrifuge tubes by washing with 5.0 mL methanol. The solution was mixed on a mechanical shaker for 20 min and centrifuged at 6000 rpm for 120 s. The supernatant was filtered through 0.45 µm syringe filters and 1.0 mL taken into vials for injection into the GC-MS system. Blank soil extracts were also sent to the instrument but fenazaquin was not detected. Unlike the irrigation water sample, the soil extract was in methanol similar to the calibration standards and this resulted in close to 100% recovery. Overlay chromatograms for 10 mg/L fenazaquin standard and irrigation canal and soil samples spiked at 10 mg/L is presented in Figure 3. The recoveries obtained for 5.0, 10 and 20 mg/kg spiked soil samples were 94.8 ± 2.2%, 101.1 ± 0.8% and 95.9 ± 1.5%. These results showed that the soil matrix did not affect recovery and quantification of fenazaquin.
Table 1 shows a comparison of the recovery percentages of fenazaquin standard at 10 mg/L in irrigation canal water and soil.

Table 1. Comparison of the recovery percentage in irrigation canal water and soil at the same concentration of fenazaquin (10 mg/L)

Sample spiked with 10 mg/L of Fenazaquin	Recovery (%)
Irrigation canal water	99.2 ± 3.0%,
Soil	101.1 ± 0.8%

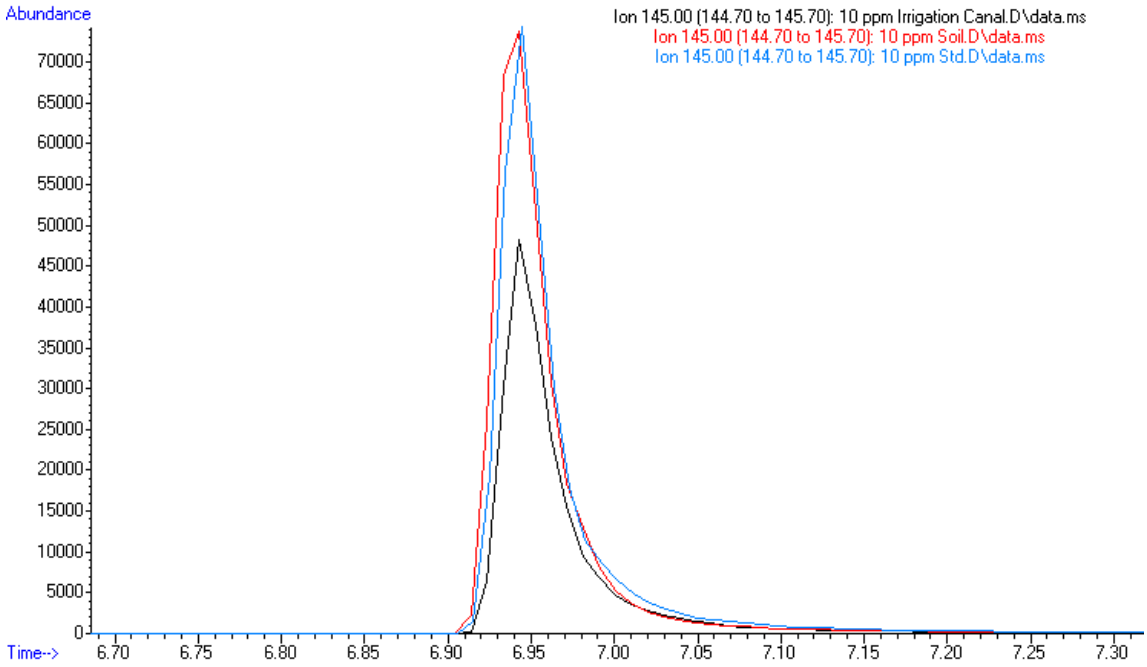

Figure 3. Overlay chromatograms of 10 mg/L standard solution, 10 mg/L spiked soil sample and 10 mg/L spiked irrigation canal water sample.

4. Conclusion

The aim of this study was to determine fenazaquin in irrigation canal water and soil samples using the highly sensitive GC-MS analytical instrument. The analyte was eluted using an appropriate temperature program within a short period and quantified based on the most intense ion. Spiked recovery studies were performed on irrigation canal water and soil samples at different concentrations to ascertain the effect of each matrix on the quantification of fenazaquin. Irrigation canal recorded low recovery results against the calibration standards but this was corrected by using matrix matching calibration technique to obtain almost 100% recovery for the three spike concentrations. The spiked soil samples produced satisfactory recovery results.

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