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Accurate and Sensitive Determination of Mefenpyr-diethyl in Barley, Oat and Corn Silk Matrices by Gas Chromatography – Flame Ionization Detector (GC–FID)

Mefenpir-dietilin Arpa, Yulaf ve Mısır Püskülü Matrikslerinde Gaz Kromatografisi - Alev İyonizasyon Dedektörü (GC-FID) ile Doğru ve Hassas Tayini

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Abstract

Pesticides are frequently utilized in the cultivation of agricultural products for human consumption to prevent / minimize the detrimental effects caused by pests and to keep the yield at the desired levels at harvest time. Besides the benefits of pesticides, unconscious use of pesticides causes the occurrence of different diseases. Monitoring the levels of pesticide residues is of vital importance for the environment, human, and other living organisms. In the present study, an analytical method was reported for the determination of mefenpyr-diethyl (MFD) as a member of the herbicide group by gas chromatography flame ionization detector (GC-FID) system with high accuracy and sensitivity. An in-column temperature program was established to effectively separate the analyte, and MFD was determined at a retention time of 5.2 min. The limit of detection (LOD), the limit of quantitation (LOQ), and the linear working range were found to be 0.01 mg/L, 0.04 mg/L, and 0.07-29.7 mg/L, respectively. The applicability of the determination method was investigated by recovery studies with barley, oat, and corn silk matrices. No analytical signal was recorded for MFD in blank samples of all three species. Recovery results close to 100% showed that MFD could be determined with high accuracy in barley, oat, and corn silk matrices.

Keywords: GC-FID, mefenpyr-diethyl, herbicide, grain matrix

Öz

İnsan tüketiminde olan zirai ürünlerin yetiştirilmesinde zararlıların neden olacağı bozucu etkileri önlemek / en aza indirmek ve hasat sırasında verimin istenen seviyelerde tutmak amacıyla pestisitlerden sıklıkla yararlanılmaktadır. Pestisitlerin faydalarının yanı sıra, bilinçsiz kullanımı farklı hastalıkların ortaya çıkmasına neden olmaktadır. Pestisit kalıntılarının seviyelerinin izlenmesi çevre, insanlar ve diğer canlı organizmalar için hayati önem taşımaktadır. Bu çalışmada, herbisit grubunun bir üyesi olan mefenpir-dietilin (MFD) gaz kromatografisi alev iyonizasyon dedektörü (GC-FID) sistemi ile yüksek doğruluk ve hassasiyetle tayini için analitik bir yöntem rapor edilmiştir. Analitin etkili bir şekilde ayrılması için kolon içi sıcaklık programı oluşturulmuş ve 5,2 dakikalık bir alıkonma süresinde MFD tayin edilmiştir. Gözlenebilme limiti (GL), tayin limiti (TL) ve doğrusal çalışma aralığı sırasıyla 0,01 mg/L, 0,04 mg/L, ve 0,07-29,7 mg/L olarak bulunmuştur. Tayin yönteminin uygulanabilirliği arpa, yulaf ve mısır püskülü örnekleri ile yapılan geri kazanım çalışmaları ile araştırılmıştır. Her üç türün kör numunelerinde MFD için analitik bir sinyal kaydedilmemiştir. %100'e yakın geri kazanım sonuçları arpa, yulaf ve mısır püskülü örneklerinde yüksek doğrulukta MFD'nin tayin edilebileceğini göstermiştir.

Anahtar Kelimeler: GC-FID, mefenpir-dietil, herbisit, tahıl matriksi

1. Introduction

Pesticides are chemicals widely used in agriculture and public health to increase crop yields by eliminating or minimizing the effects of pests (Ross and Carr 2019). In addition to their role in preventing diseases, pesticides are also preferred in agriculture both before and after harvesting to improve the quality and quantity and to enhance the storage period of agricultural products (Chormey 2021, Durak et al. 2020, Weiss et al. 2004). However, over the years, detrimental effects on the health of humans and other living things have been identified due to DDT (dichlorodiphenyltrichloroethane) usage, and therefore scientists have focused on the

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development of pesticides that are more environmentally friendly (Rosini et al. 2008, Umetsu and Shirai 2020). Parameters such as chemical structure, target organism, mode of application, mechanism of action, organic/inorganic and natural/synthetic type are prominent in the classification of pesticides (Chormey et al. 2017). Pesticides are grouped as fungicides, insecticides, and herbicides, depending on the target organisms (Lushchak et al. 2018). Among them, herbicides are a type of pesticide that has been widely used to control of weeds growing in crop and non-crop areas since about the 1940s (Kettles et al. 1997). It has been reported that herbicides have a global share of approximately 50% in the pesticide class. Besides crop areas, herbicides are often preferred to eliminate aquatic plants in the lake, weeds that grow on the side of the road and shrub-derived plants (Yang et al. 2021). Uncontrolled use of herbicides in agricultural applications not only causes environmental pollution by contaminating the soil and water resources, but also the accumulation of herbicide residues in aquatic environments and soil poses a risk to the living life using these environments (Li et al. 2023). The harmful impacts of herbicides on human and living organisms' health depend on various factors including the type of chemicals, the amount of consumption, the duration and the type of exposure (Aparecida et al. 2013). It has been reported that long-term exposure to these substances can cause a range of health consequences such as neurodegenerative diseases, cancer, and reproductive and respiratory problems (Maes et al. 2021).

Mefenpyr-diethyl (MFD), a member of the herbicide group, is a chemical belonging to the pyrazoline group and is a preservative used in combination with different herbicides to reduce the effect of weed species in the cultivation of grain crops such as barley, oats, wheat, and triticale (Bianchi et al. 2021). It has been reported that MFD is effective on plant growth and being protective, but its excessive dose causes the drying of plant roots (Taylor et al. 2013). The American Society of Plant Biologists has reported MFD as an herbicide with carcinogenic effects. Due to its carcinogenic potential, the arrival of this herbicide in resources such as water and soil is a cause for concern to the public and regulatory agencies (El Boukili et al. 2018). For this reason, qualitative and quantitative determination of MFD concentration in ground and surface water samples, soil samples, and human consumption food samples is crucial for monitoring these effects and taking precautions.

Chromatography, which is widely used in the separation and qualitative and quantitative determination of pesticides and other organic molecules, is categorized under two headings according to the type of mobile phase as gas chromatography (GC) (Erarpat et al. 2019) and liquid chromatography (LC) (Tekin et al. 2023). Among these methods, GC is an analytical method with a high capability in separating volatile organic compounds. The several detector types such as nitrogen phosphorus detector (NPD) (Tian et al. 2014), thermal conductivity detector (TCD) (Budiman et al., 2015), electron capture detector (ECD) (Tandon et al. 2015), mass spectrometry (MS) (Kapukıran et al. 2019), flame photometric detector (PID) (Sun et al. 2014) and flame ionization detector (FID) (de Souza Pinheiro and de Andrade 2009) are generally utilized in the GC system for the determination of pesticides. Here, GC-FID was applied in the method development studies.

The main objective of this study was to determine the MFD in barley, oat, and corn silk matrices with high accuracy in the GC-FID system. Since herbicides containing MFD are frequently used to control weeds in barley, oats and wheat cultivation in the fields, these grain samples were selected as real samples for qualitative/quantitative determination of herbicide residues. The recovery studies confirmed the applicability of the applied method carried out with these samples.

2. Material and Methods

2.1. Instrumentation

An Agilent 6890N model gas chromatography system and flame ionization detector were employed in the separation/determination of MFD. The Chemstation software, which is compatible with the GC-FID system, was used to display, evaluate, and record the analytical data obtained. The hydrogen gas required for the system was supplied from the Domnick Hunter model 40H hydrogen generator. The length, film thickness and inner diameter of the column (HP-5MS) utilized in the separation of MFD were defined as 30 m, 0.25 µm, and 250 µm, respectively. The detector and inlet temperatures were kept constant at 250 °C. The sample volume injected into the system in splitless mode was 1.0 µL. The oven temperature program was set in ramp mode to ensure the effective separation in 6.1 minutes as follows: From 100 °C to 220 °C in 50 °C/min increments, from 220 °C to 270 °C in 30 °C/min increments with 2.0 minutes of hold time. In the sample preparation step, a vortex (Isolab) and an ultrasonic bath (Alex Machine) were used for the mixing process. The phase separation was achieved by employing a centrifuge (Hettich-EBA20) at 3000 rpm.

A four-digit analytical balance (OHAUS PA214C) was utilized throughout all standard/sample preparations.

2.2. Chemicals and Reagents

High purity mefenpyr-diethyl (CAS: 135590-91-9) was obtained from Dr. Erhrenstorfer (Germany). 1000 mg/L stock standard MFD solution was prepared in acetonitrile (Isolab). Gravimetrical dilution of the stock solution was carried out with acetonitrile to prepare MFD standard solutions at different concentrations. 10 µL ethanol (Isolab) was used to wash the injection unit that feeds the sample into the system.

2.3. Samples

The barley, oat and corn silk samples used in the recovery studies were purchased from a local herbalist in İstanbul, Türkiye. 1.0 g of barley and oat samples whose surface areas were increased by crushing and grinding processes were weighed and diluted to 5.0 g with 5.09 mL of acetonitrile. 0.50 g of the corn silk sample, whose surface area was increased by cutting with sterile scissors, was weighed, and diluted to 5.0 g with 5.73 mL of acetonitrile. All three samples were extracted by mixing in 60 s vortex and 60 s ultrasonic bath, respectively and then used as blank samples after centrifugation and filtration. The prepared solutions were spiked to final concentrations of 2.5, 5.0 and 10 mg/L for recovery studies.

3. Results and Discussion

3.1. Qualitative and Quantitative Determination of MFD

All MFD calibration standard solutions were analyzed in triplicate under the temperature program and operating conditions given in Section 2.1 to investigate the accuracy, precision, and applicability of the proposed method. The retention time for MFD was recorded as 5.2 min (Figure 1) and the nine-point calibration plot was obtained based the mean peak areas. The linear dynamic range was determined between 0.07 and 29.7 mg/L with a coefficient (R^2) of 1.0000. The lowest concentration with a signal-to-noise ratio ≥ 3 was sent to the GC-FID system six times, and the obtained standard deviation value was employed in the following formulas given in Equations 1, 2, and 3 to calculate the limit of detection (LOD), the limit of detection (LOQ), and percent relative standard deviation (RSD%) and these values found to be 0.01 mg/L, 0.04 mg/L and 8.7%, respectively (Serbest et al. 2023, Yağmuroğlu 2023):

$$LOD = 3 \times \text{Standard deviation} / \text{Slope of calibration plot} \quad (1)$$

$$LOQ = 10 \times \text{Standard deviation} / \text{Slope of calibration plot} \quad (2)$$

$$RSD\% = 100 \times \text{Standard deviation} / \text{Mean} \quad (3)$$

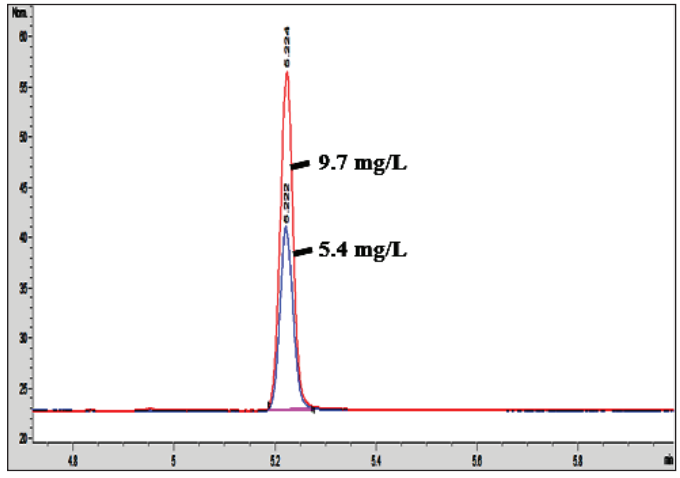

Figure 1. The overlay chromatograms of MFD standard solutions under proposed GC-FID conditions.

The MFD standard solution with a concentration of 5.4 mg/L was analyzed on three different days to investigate the precision of the GC-FID system. The RSD% between the obtained peak areas was close to 6.5%. This result showed that the GC-FID system has high repeatability for the determination of MFD. The analytical performance values of the GC-FID system for MFD determination under the proposed conditions are summarized in Table 1.

3.2. Recovery Studies in Real Samples

Pesticides are complex substances widely used in agricultural areas to prevent or reduce the effects of harmful organisms and pose a risk to human health and other living organisms (Özcan et al. 2020). Pesticide residues can be found

Table 1. System analytical performance values of GC-FID for MFD determination.

Analyte	LOD, mg/L	LOQ, mg/L	Linear Range, mg/L	R^2	RSD%
Mefenpyr-diethyl	0.01	0.04	0.07 – 29.7	1.0000	8.7

in products that reach the market from the field. Therefore, it is critical to perform qualitative/quantitative determinations of these products with high accuracy. In order to investigate the applicability of the proposed method, recovery studies were carried out on barley, oat and corn silk matrices. MFD has high solubility in acetonitrile. Hence, barley, oat and corn silk samples were extracted with acetonitrile as mentioned in the "Samples" section. Extracted samples were injected to the GC-FID system as blank solutions and the presence of MFD was investigated, but no analytical signal was observed in all three samples. After blank analysis, spiked samples were carefully prepared at 2.5, 5.0 and 10 mg/L and percent recovery values were calculated by external calibration method after four replicates measurements. The recovery results are presented in Table 2.

Table 2. Recovery results for barley, oat, and corn silk matrices

Sample	Spiked Concentration, mg/L	External Calibration Recovery ± Std. Dev., %
Barley	2.5	101.8 ± 4.7
	5.0	98.9 ± 1.3
	10	99.8 ± 1.2
Oat	2.5	104.3 ± 3.6
	5.0	103.4 ± 3.1
	10	101.2 ± 1.3
Corn Silk	2.5	97.6 ± 1.8
	5.0	101.5 ± 4.8
	10	101.0 ± 2.7

4. Conclusion and Suggestions

Within the scope of this study, an analysis method was presented in the GC-FID system for the direct determination of mefenpyr diethyl herbicide in barley, oat, and corn silk matrices. A gradual temperature program was applied to determine the MFD in a run time of 6.1 min. Under the specified conditions, the LOD value was found to be 0.01 mg/L with an 8.7% RSD. The applicability of the proposed method in real samples was evaluated with recovery experiments by spiking for three different concentrations using barley, oat, and corn silk samples. Satisfactory percentage recovery results achieved between 97.6% and 104.3% with low standard deviations indicated the feasibility and the accuracy of the developed method for these grain matrices. Thanks to the presented method, MFD, which is used especially for the removal of weeds in grain cultivation, can be determined with high accuracy.

Author contribution: Hakan Serbest: Conceptualization, Formal analysis, Data curation, Methodology, Investigation, Validation, Visualization, Writing.

Ethics committee approval: No ethical approval is required.

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