Karaelmas Science and Engineering Journal
Journal home page: https://dergipark.org.tr/tr/pub/karaelmasfen
DOI: 10.7212/karaelmasfen.1770790

Research Article
Received / Geliş tarihi : 22.08.2025
Accepted / Kabul tarihi : 11.10.2025

Sensitive and Selective Determination of Chlorfenson in Drinking Water Using Gas Chromatography-Mass Spectrometry

Gaz Kromatografisi-Kütle Spektrometrisi Kullanılarak İçme Sularında Chlorfenson'un Hassas ve Seçici Tayini

Merve Fırat Ayyıldız

İstanbul Gelişim University, Vocational School of Health Care Services, Department of Food Quality Control and Analysis, İstanbul, Türkiye

Abstract

In this study, the pesticide chlorfenson was determined and quantified in drinking water samples using gas chromatography-mass spectrometry (GC-MS). An optimized temperature program enabled the elution of chlorfenson with a sharp, transient peak and a short total run time of 7.0 minutes. Identification and quantification of chlorfenson were based on ion peaks with high relative abundance selected from the National Institute of Standards and Technology (NIST) library, with confirmation of the specific chromatographic peak. The method showed linearity across a broad concentration range (0.52– 49.53 mg/kg), with a limit of detection (LOD) of 0.17 mg/kg and a limit of quantification (LOQ) of 0.56 mg/kg. Method validity was confirmed through recovery experiments on real drinking water samples. Although chlorfenson was not detected in the tested drinking water samples, spiked samples showed recovery rates ranging from 87.6% to 123.3%. These results demonstrate that the proposed method provides accurate and reliable determination of chlorfenson in complex matrices such as drinking water that can support routine monitoring and enable future enhancements in sensitivity through integration with preconcentration techniques.

Keywords: Chlorfenson, drinking water, gas chromatography, pesticide.

Öz

Bu çalışmada, klorfenson adlı pestisitin içme suyu örneklerinde gaz kromatografisi-kütle spektrometresi (GC-MS) yöntemiyle belirlenmesi ve miktar tayini yapılmıştır. Analiz sırasında klorfensonun etkin şekilde ayrılabilmesi için uygun bir sıcaklık programı uygulanmış ve toplam analiz süresi 7.0 dakika olarak optimize edilmiştir. Klorfensonun tanımlanması ve kantifikasyonu için Ulusal Standartlar ve Teknoloji Enstitüsü (NIST) kütüphanesinden seçilen yüksek bağıl bolluğa sahip iyon pikleri kullanılmış, kromatogramdaki spesifik pik kimliklendirilmiştir. Yöntem, 0.52 mg/kg ile 49.53 mg/kg arasında geniş bir doğrusal aralıkta çalışabilmektedir. Gözlenebilme limiti (LOD) 0.17 mg/kg, tayin limiti (LOQ) ise 0.56 mg/kg olarak tespit edilmiştir. Geliştirilen yöntemin gerçek içme suyu örneklerinde yapılan geri kazanım testleri ile geçerliliği onaylanmıştır. Test edilen içme suyu örneklerinde klorfenson bulunmazken, standart ilaveli numunelerde yapılan deneylerde geri kazanım oranları %87.6 ile %123.3 arasında değişmiştir. Bu sonuçlar, önerilen yöntemin içme suyu gibi karmaşık matrislerde klorfensonun doğru ve güvenilir bir şekilde belirlenmesini sağladığını, rutin gözetimi destekleyebileceğini ve ön konsantrasyon işlemleri yoluyla gelecekteki hassasiyet artışları için bir platform sağlayabileceğini göstermektedir.

Anahtar Kelimeler: Gaz kromatografisi, içme suyu, klorfenson, pestisit.

*Corresponding author: merve.f@yahoo.com

Merve Fırat Ayyıldız orcid.org/0000-0003-3523-8169

1. Introduction

Pesticides are chemicals or mixtures widely used in agriculture and public health to protect crops from pests, weeds, and diseases, as well as to mitigate human exposure to vector-transmitted illnesses like schistosomiasis, malaria, and dengue fever (Nicolopoulou-Stamati et al., 2016). Given their functional properties, pesticides can harm not only the intended pests but also non-target species, including humans. The World Health Organization (WHO) estimates that around 3 million people are affected by pesticide poisoning annually, resulting in up to 220,000 fatalities, mostly in developing nations (Singh et al., 2018). Prolonged direct or indirect contact with pesticides has been associated with a range of health issues, including reproductive system disorders, respiratory diseases, heart-related conditions, digestive system problems, and neurological disorders (Shekhar et al., 2024). Pesticide occurs via both direct and indirect pathways. Direct exposure involves personal application of pesticides in environments such as homes, workplaces, or agricultural fields, typically leading to higher levels of contact. In contrast, indirect exposure occurs via contaminated air, dust, food, or drinking water, usually resulting in prolonged, low-level exposure, which may actually occur more often than direct contact (Upadhayay et al., 2020).

Chlorfenson, chemically known as Benzenesulfonic acid, 4-chloro-4-chlorophenyl ester, is a non-corrosive white crystalline solid with a melting point of 86.5 °C (Ramalingam et al., 2013). The molecular weight of chlorfenson is 303.2 g/mol (*Chlorfenson | $C_{12}H_8Cl_2O_3S$ | CID 6635 - PubChem*, n.d.). It belongs to the sulfonate class of compounds and serves as an active ingredient in plant protection formulations. Functioning as both an insecticide and acaricide, chlorfenson is notable for its long-lasting ovicidal effect. It is primarily used to control mites on crops such as citrus fruits, vegetables, ornamental plants, and other fruits (Aydin et al., 2023; Ramalingam et al., 2013).

Chromatography is a commonly used analytical technique for separating complex chemical mixtures into their individual pure substances. The instrument/device used for this process is called a chromatograph. Various types of chromatography exist, including thin-layer chromatography (TLC), liquid chromatography (LC), and gas chromatography (GC). Although they differ in application, they all operate on shared fundamental chemical principles (Gaffney and Marley, 2018). Gas chromatography is a versatile technique in analytical chemistry, primarily applied for the separation and analysis of volatile organic compounds. Critical steps such as sample preparation, possible derivatization, and optimization of instrument parameters are typically required for accurate and reliable results (Wongsa and Rattanapanone, 2023). Gas chromatography combined with mass spectrometry is particularly effective for detecting and identifying volatile and thermally stable compounds. Mass spectrometry stands out as one of the most commonly utilized identification techniques due to its superior sensitivity and selectivity (Fernández et al., 2024). Compared to liquid chromatography, gas chromatography provides benefits including improved separation performance, reduced interference from matrix components, and more accessible and dependable reference mass spectral data (Devers et al., 2025).

The aim of this study was to determine chlorfenson residues in drinking water using a gas chromatography mass spectrometry system with high analytical accuracy. Given its classification as a pesticide and its potential risk for environmental contamination, chlorfenson was selected as the target analyte. Commercially available drinking water was analyzed to perform both qualitative and quantitative residue assessments. Recovery experiments conducted on these samples were used to evaluate the practicality and reliability of the developed method. Consequently, this work addresses a practical need for a simple, direct GC-MS protocol to determine chlorfenson in drinking water without labor-intensive pretreatment. The study's contribution is to construct a compact, instrument-only workflow that demonstrates linear response, method trueness across spiking levels, and suitability for routine applications. The method to be developed may also be a foundation for subsequent formal validation and integration with preconcentration techniques to extend sensitivity when required.

2. Material and Methods

2.1. Instrumentation and Chromatographic Conditions

Qualitative and quantitative analyses of chlorfenson were performed using an Agilent gas chromatograph (model 6890 N) equipped with an HP-5MS capillary column (30 m × 250 μm ID × 250 nm film thickness) for analyte elution. Helium (99.999% purity) was used as carrier gas, delivered at a flow rate of 60 mL/min. The GC system was interfaced with an Agilent mass spectrometer (model 5973 N), enabling both identification and quantification of chlorfenson. The inlet temperature was maintained consistently at 280°C throughout the analysis. In the first trial, the temperature program was set to achieve effective elution within a total

runtime of 10 minutes, starting at 100°C and ramping at 30°C /min to a final temperature of 300°C. A final hold time of 3.33 minutes was applied. In the second trial, to obtain efficient elution within a total runtime of 6 minutes, the temperature program was initiated at 120°C and increased at a rate of 30°C /min to a final temperature of 280°C, with a final hold time of 0.67 minutes. Finally, under the optimum condition, the temperature program was optimized to achieve effective elution within a total runtime of 7.0 minutes, starting at 100°C and ramping at 30°C/min to a final temperature of 280°C. Under these conditions, the best separation performance was obtained. In all experiments, the optimized operating parameters were kept constant: an ion source temperature of 230°C, a splitless injection volume of 1.0 µL, a transfer line temperature of 280°C, and a quadrupole temperature of 150°C.

Standard and sample solutions were prepared gravimetrically using a high-precision analytical balance (Shimadzu, Japan).

2.2. Reagents and Chemicals

The chlorfenson stock standard was obtained from Dr. Ehrenstorfer GmbH (Germany). Calibration standards were prepared by gravimetric dilution of the stock standard with acetonitrile on an analytical balance. Acetonitrile (purity ≥ 99.8%) was supplied by Merck (Darmstadt, Germany). Chlorfenson solutions at concentrations of 0.52, 1.04, 2.00, 5.01, 7.67, 10.94, 20.28, 49.53, and 99.78 mg/kg were stored at +4 °C until analysis.

2.3. Sample Preparation

For the recovery experiments, bottled drinking water samples of two different brands purchased from markets in Istanbul were used. From each water sample, 0.25 g was precisely weighed into vials using an analytical balance. Subsequently, chlorfenson standard was added to the samples at varying concentration levels, after which the total sample weight was adjusted to 1.0 g with acetonitrile. The mixtures were gently shaken until homogenous. These spiked samples were used in recovery experiments to evaluate the accuracy of the method.

3. Results and Discussion

3.1. Qualitative and Quantitative Determination of Chlorfenson

Chlorfenson was identified and qualified by evaluating a distinct and sharp chromatographic peakobtained from the extraction of its five dominant m/z ion fragments. In the chromatogram, a peak at 5.53 minutes was matched to chlorfenson in the NIST mass spectral library with a match quality of 99% (Figure 1). Following identification, the system's performance for chlorfenson analysis was evaluated.

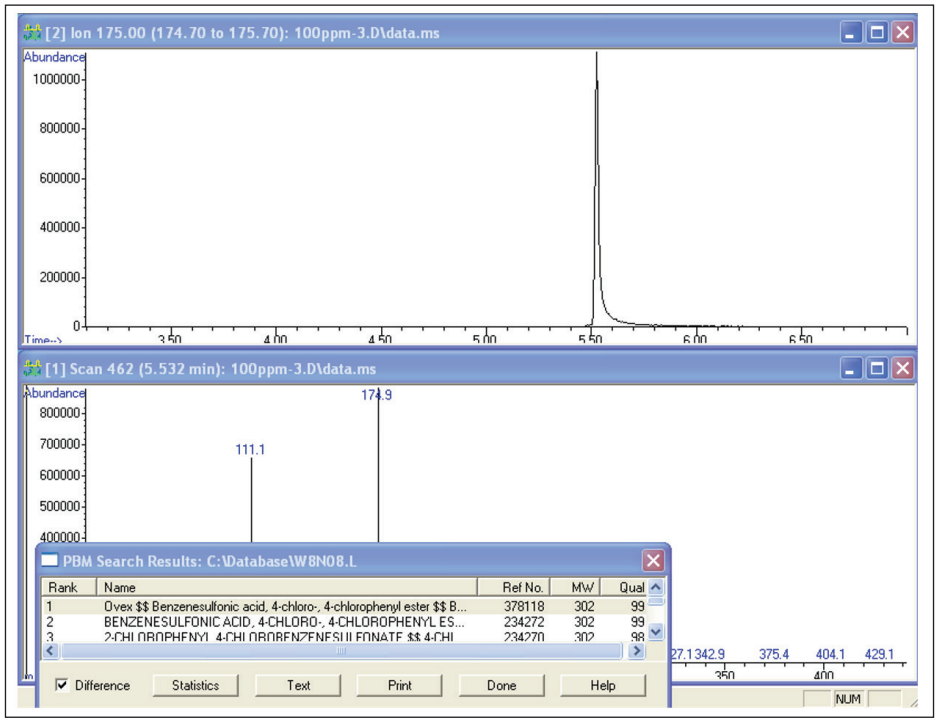

Figure 1. GC–MS fragmentation pattern of chlorfenson, highlighting the major *m/z* ion peaks.

Calibration standards covering a concentration range of 0.52 – 99.78 mg/kg were prepared and analyzed under identical instrumental conditions, with a minimum of four replicate injections for each concentration. For quantification, the m/z 175 ion fragment, which is the most intense signal among chlorfenson's fragments was selected, and peak areas were determined manually using ChemStation software. Signal intensity showed a proportional increase with chlorfenson concentration (Figure 2).

For each concentration level, the average peak area was calculated and plotted against the corresponding chlorfenson concentrations to generate a calibration curve. The method exhibited good linearity over the linear working range (LWR) range of 0.52 – 49.53 mg/kg, with a coefficient of determination (R^2) of 0.9996 (Figure 3).

The limit of detection (LOD) and limit of quantification (LOQ) were determined using the standard approach: threefold and tenfold, respectively, the standard deviation of six replicate measurements at the lowest calibration level, divided by the slope of the calibration curve. Based on this calculation, the LOD and LOQ were 0.17 mg/kg and 0.56 mg/kg, respectively. A analytical performance characteristics of the GC-MS method for chlorfenson are listed in Table 1.

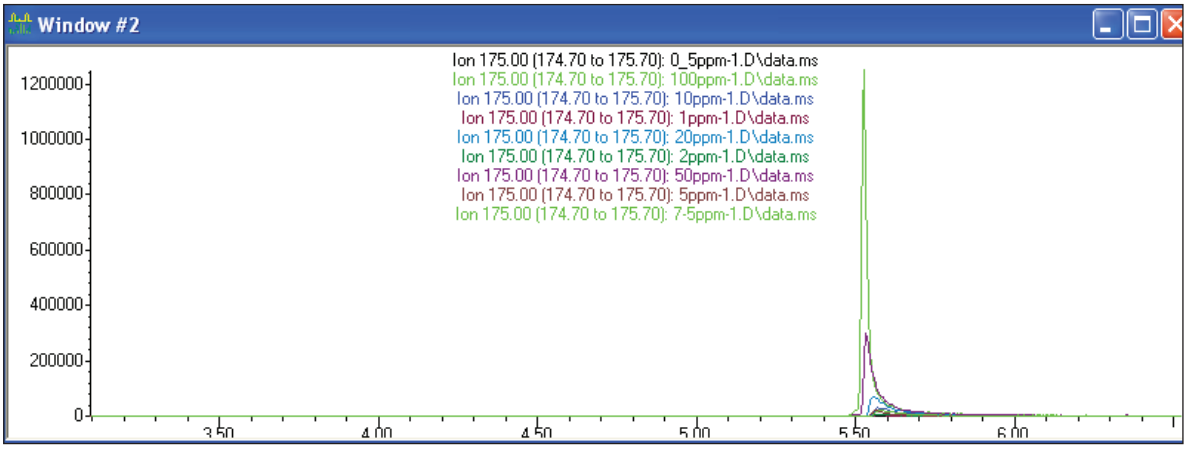

Figure 2. Overlay plot of selected ion chromatograms for chlorfenson with different concentration values.

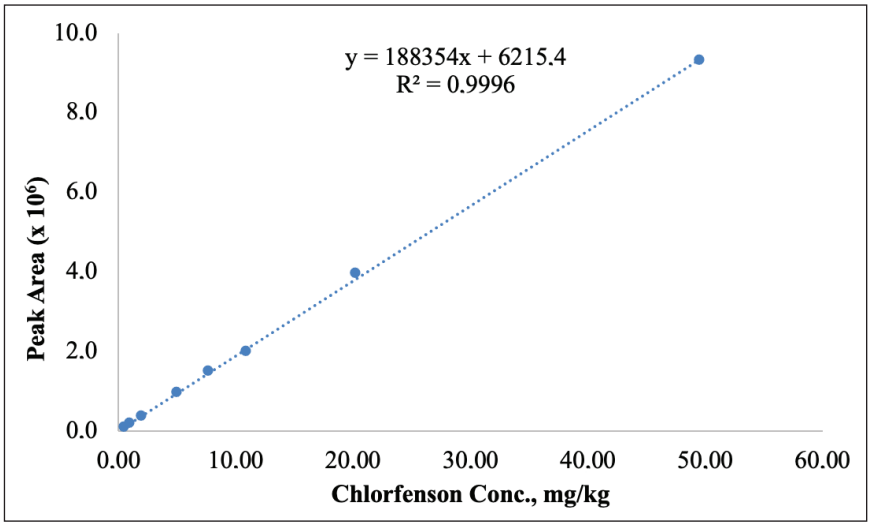

Figure 3. Relationship between chlorfenson concentrations and corresponding peak areas, demonstrating method linearity.

Table 1. The analytical figures of merit of the developed analytical method.

Analyte	LOD, mg/kg	LOQ, mg/kg	LWR, mg/kg	R^2
Chlorfenson	0.17	0.56	0.52-49.53	0.9996

3.2. Recovery Studies in Real Samples

The increasing reliance on chemical inputs to enhance agricultural productivity and improve harvest quality, along with large-scale industrial productions to meet the demands of a rapidly growing human population, has led to the contamination of environmental resources such as water, air, soil, and forests. This has raised concerns over pesticide residue levels and their potential risks to human health (Chormey et al., 2020; Zeng et al., 2024).

Recovery studies were carried out on drinking water samples purchased from markets in İstanbul to evaluate the accuracy of the analytical method.

An initial analysis of the drinking water samples was performed but no detectable signal was found in either of the two tested samples. The samples were then spiked with chlorfenson at approximate concentrations of 2, 5, 7.5, 10, and 20 mg/kg, and each level was analyzed in four replicate measurements.

Initial recovery percentages were calculated using the external calibration method. For this, the linear regression equation (y=169948x + 60332), derived from the standard calibration curve under identical instrumental conditions, was used to estimate the concentrations of the spiked samples. However, the recovery values obtained by this approach were unsatisfactory, likely due to matrix differences between the calibration standards and the actual sample matrix. To overcome this limitation and improve accuracy, recovery calculations were repeated using the matrix matching calibration technique. Matrix matching is performed by preparing calibration standards in a blank sample matrix that closely resembles the composition of the actual test samples, rather than in pure solvent. This compensates for matrix-induced signal suppression or enhancement, ensuring more accurate quantification.

The recovery results for two water brands using the matrix matching technique were in the acceptable range of 87 – 124% (Table 2).

Table 2. Percent recoveries of chlorfenson in two drinking water brands determined by matrix-matching.

Sample	Spike Concentration, mg/kg	Matrix Matching Recovery ± Std. Dev., %
Drinking Water A	1.96	112.4 ± 8.0
	5.00	89.1 ± 4.5
	7.04	108.7 ± 14.9
	9.40	110.9 ± 9.8
	19.54	115.5 ± 4.2
Drinking Water B	1.93	123.3 ± 6.7
	4.40	98.0 ± 7.2
	6.50	94.0 ± 7.3
	10.23	87.6 ± 4.4
	19.61	88.1 ± 4.6

4. Conclusion and Suggestions

In this study, chlorfenson in drinking water was determined using a GC-MS system. An appropriate temperature program enabled efficient elution of the analyte through the capillary column within 7.0 minutes for detection by the mass spectrometry detector. The method exhibited a limit of detection of 0.17 mg/kg, and a limit of quantification of 0.56 mg/kg. In order to check the applicability and accuracy of the method developed, recovery experiments were performed by spiking chlorfenson at different concentration levels. Recovery values in the range of 87 – 124% demonstrated the accuracy and reliability of the developed method. Overall, the results provide a compact basis for routine monitoring. The results of this study can be further leveraged to pursue formal validation emphasizing robustness and inter-laboratory reproducibility and to couple the workflow with selective preconcentration strategies to lower detection limits while maintaining quantitative performance.

5. Acknowledgment

The author sincerely thanks the Bakırdere Research Group at Yıldız Technical University for granting access to the facilities necessary to conduct this research.

Author contribution: Merve Fırat Ayyıldız: Conceptualization, Formal analysis, Data curation, Methodology, Investigation, Validation, Visualization, Supervision, Writing – original draft, review & editing.

Ethics committee approval: No ethical approval is required.

Conflict of interest: The author declares that there is no conflict of interest.

6. References

Aydin, N., Tekin, Z., Turan, NB., Bakırdere, S. 2023. Development of a vortex-assisted dispersive micro-solid-phase extraction using reduced graphene oxide/Fe_3O_4 nanocomposites for the determination of chlorfenson pesticide in green tea samples by high-performance liquid chromatography-ultraviolet detection. Chemical Papers, 77(4): 2141–2149. Doi: 10.1007/s11696-022-02616-z

Chormey, DS., Fırat Ayyıldız, M., Bakırdere, S. 2020. Feasibility studies on the uptake and bioaccessibility of pesticides, hormones and endocrine disruptive compounds in plants, and simulation of gastric and intestinal conditions. Microchemical Journal, 155: 104669. Doi: 10.1016/j.microc.2020.104669

Devers, J., Pattison, DI., Hansen, AB., Christensen, JH. 2025. Comprehensive two-dimensional gas chromatography as a tool for targeted and non-targeted analysis of contaminants of emerging concern in wastewater. Talanta, 282: 127032. Doi: 10.1016/j.talanta.2024.127032

Fernández, PC., Duque, MJT., Freire, IÁ., Barrera, AMB. 2024. Gas chromatography methods. Comprehensive Analytical Chemistry. Doi: 10.1016/bs.coac.2024.11.012

Gaffney, JS., Marley, NA. 2018. Chemical Measurements and Instrumentation. General Chemistry for Engineers, 493–532. Doi: 10.1016/b978-0-12-810425-5.00015-1

Nicolopoulou-Stamati, P., Maipas, S., Kotampasi, C., Stamatis, P., Hens, L. 2016. Chemical Pesticides and Human Health: The Urgent Need for a New Concept in Agriculture. Frontiers in Public Health, 4: 178764. Doi: 10.3389/fpubh.2016.00148

Ramalingam, S., Periandy, S., Sugunakala, S., Prabhu, T., Bououdina, M. 2013. In silico molecular modeling, docking and spectroscopic [FT-IR/FT-Raman/UV/NMR] analysis of chlorfenson using computational calculations. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 115: 118–135. Doi: 10.1016/j.saa.2013.06.034

Shekhar, C., Khosya, R., Thakur, K., Mahajan, D., Kumar, R., Kumar, S., Sharma, AK. 2024. A systematic review of pesticide exposure, associated risks, and long-term human health impacts. Toxicology Reports, 13: 101840. Doi: 10.1016/j.toxrep.2024.101840

Singh, NS., Sharma, R., Parween, T., Patanjali, PK. 2018. Pesticide Contamination and Human Health Risk Factor. Modern Age Environmental Problems and Their Remediation, 49–68. Doi: 10.1007/978-3-319-64501-8_3

Upadhayay, J., Rana, M., Juyal, V., Bisht, SS., Joshi, R. 2020. Impact of pesticide exposure and associated health effects. Pesticides in Crop Production: Physiological and Biochemical Action, 69–88. Doi: 10.1002/9781119432241.ch5

Wongsa, P., Rattanapanone, N. 2023. Gas chromatography and multivariate analysis for wheat flours. Food Quality Analysis: Applications of Analytical Methods Coupled with Artificial Intelligence, 149–169. Doi: 10.1016/b978-0-323-95988-9.00008-4

Zeng, Y., Lan, T., Li, X., Chen, Y., Yang, Q., Qu, B., Zhang, Y., Pan, C. 2024. A comparison of the determination of multiple pesticide residues in fruits, vegetables, and edible fungi using gas chromatography combined with filtration purification and solid-phase extraction. RSC Advances, 14(24): 16898–16911. Doi: 10.1039/d3ra07584b