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Determination of Prosulfocarb in Potato Flour Samples by Gas Chromatography-Mass Spectrometry

Prosülfokarbın Gaz Kromatografisi-Kütle Spektrometrisi ile Patates Unu Örneklerinde Tayini

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Abstract

In this study, a gas chromatography-mass spectrometry (GC-MS) method was developed for the detection of prosulfocarb in potato flour matrix. GC-MS parameters were elaborately evaluated to achieve well-separated analyte signal with high signal to noise ratio. Under the optimum instrumental conditions, the limits of detection and quantification (LOD and LOQ) were found as 0.54 mg/kg and 1.80 mg/kg, respectively, which facilitates the determination of prosulfocarb at ppm levels. The established method was applied to potato flour samples spiked to six different concentration levels (2.6–101.7 mg/kg). Blank analyses were also performed for three different brand samples but prosulfocarb were found in the samples below the detection limit. Satisfactory percent recoveries between 90.9 and 105.7% with %RSD (≤3,6%) were acquired for the selected sample matrix. High recoveries obtained with the matrix matching calibration strategy proved the accuracy and applicability of the developed method while low %RSD value showed the precision of the analytical method. It is suggested that the established method can be used to detect ppb/ppt levels of the analyte after a preconcentration method was applied to the sample solutions.

Keywords: GC-MS, matrix matching calibration method, potato flour, prosulfocarb.

Öz

Bu çalışmada, patates unu örneklerinde prosülfokarbın tayini için bir gaz kromatografisi-kütle spektrometresi (GC-MS) yöntemi geliştirilmiştir. Yüksek sinyal/gürültü oranına sahip iyi ayrılmış analit sinyali elde etmek için GC-MS parametreleri ayrıntılı bir şekilde değerlendirilmiştir. Optimum enstrümantal koşullar altında, gözlenebilme ve tayin limitleri (GL ve TL) sırasıyla 0,54 mg/kg ve 1,80 mg/kg olarak bulunmuştur, bu da prosülfokarbın ppm seviyelerinde belirlenmesine imkân tanımaktadır. Belirlenen yöntem, altı farklı konsantrasyon seviyesinde (2,6-101,7 mg/kg) standart eklenen patates unu örneklerine uygulanmıştır. Üç farklı marka örnek için kör analizler yapılmış ancak prosülfokarb, tespit limitinin altında bulunmuştur. Seçilen örnek matriksi için %RSD (≤%3,6) ile %90,9 ile %105,7 arasında kabul edilebilir yüzde geri kazanımlar elde edilmiştir. Matriks eşleştirme kalibrasyon stratejisi kullanılarak elde edilen yüksek geri kazanımlar, geliştirilen yöntemin doğruluğunu ve uygulanabilirliğini kanıtlarken, düşük %RSD değerleri analitik yöntemin kesinliğini göstermiştir. Örnek çözeltilerine ön deriştirme yöntemi uygulandıktan sonra analitin ppb/ppt seviyelerini tespit etmek için oluşturulan yöntemin kullanılabileceği önerilmektedir.

Anahtar Kelimeler: GC-MS, matriks eşleştirme kalibrasyon yöntemi, patates unu, prosülfokarb.

1. Introduction

Herbicides are substances applied to kill, control or prevent excessive growth of weeds or unwanted plants (Hormenoo et al. 2021). These substances are important chemicals used in agriculture, industry, domestic and commercial areas (Bo et al. 2020). Among these chemicals, thiocarbamates have been used as herbicides (Guarda et al. 2020), insecticides (Lee et al. 2004) and fungicides (Gnatyshyna et al. 2020). These molecules with S-benzyl, S-alkyl or S-chlorobenzyl group are converted into sulfoxides in mammalian and plant bodies (Bo et al. 2020). Prosulfocarb (S-benzyl dipropylthiocarbamate) is used as herbicide for winter cereals (Nègre et al. 2006). It was discovered by Stauffer Chemical in Belgium in the late of 1980s (Shaner 2014). In European countries, prosulfocarb is used to selectively control grass and broad-leaved weeds in potatoes and winter

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wheat (European Food Safety Authority 2007). It has low water solubility (~10 mg/L) that reduces the possibility of leaching downward (Nègre et al. 2006). It has been detected higher than 1.0 ng/m^3 in atmosphere in France (Villiot et al. 2018) and detected in two different sampling location in Denmark (Ellermann et al. 2012, Muñoz et al. 2018). In literature, acceptable daily intake for human bodies is 0.005 mg/kg body weight per day (Devault et al. 2022). Although prosulfocarb effect on human health is not deeply highlighted in literature, thiocarbamate herbicides can be metabolized and reacted with biologically active compounds that impairs important cell processes. In addition, these chemicals can easily pass into cell membranes and physiological barriers like blood-brain and fetal placental barriers due to their lipophilic nature (Mathieu et al. 2015). For this reason, determination of prosulfocarb in food samples is an important issue for human health and environment.

In literature, prosulfocarb has been generally separated and detected by high performance liquid chromatography (HPLC) (Gennari et al. 2002, Marín-Benito et al. 2018). However, gas chromatography (GC) is a powerful instrumental method for volatile and semi-volatile analytes. It has many detector options to obtain sensitive, selective and specific analyte detection (Erarpat et al. 2020). Among them, mass selective detector (MS) is a prominent instrumental method as a detector for GC systems because it gives the number of analyte and their concentration in a sample and structural information of analytes as well (Stauffer 2013). LC-MS systems needs hazardous solvents as mobile phases but GC-MS has no problem about mobile phase issues (Sparkman et al. 2011). In addition, GC-MS has a great advantage of having library based-sample identification that provides compound names, molecular structure, elemental formula (Tsizin et al. 2017). Hence, GC-MS system was performed in the presented study for the quantification of prosulfocarb in potato flour samples.

Calibration is one of the most important steps in any analytical procedure. In ideal conditions, calibration standards and sample solutions have similar matrix medium. It is difficult to perform calibration process if the sample matrix is less similar to calibration standards or more complicated (Sloop et al. 2019). Matrix effects can be minimized by matrix matching calibration method meaning that the matrix of the calibration standards is adjusted to match the matrix of the sample (Vogl 2005). The matrix-matched calibration plot was constructed via the spiked sample solution. In this method, the sample solution used during the construction of calibration plot should be analyzed and not contain target analyte (Bodur et al. 2024). Matrix matching calibration method was used during the recovery experiments of prosulfocarb in order to alleviate matrix effects.

Potato (*Solanum tuberosum L.*) ranks fourth after wheat, rice and corn in terms of production volume among various agricultural products in the world. The total potato cultivation area in Turkey is 203,000 hectares and a total of 5,250,000 tons of potatoes are produced (Ünlü et al. 2006). According to Republic of Türkiye Ministry of Agriculture and Forestry, prosulfocarb is used at high concentration levels (800 g/L with 400-500 mL/da) for barley, wheat and potato (Tarım ve Orman Bakanlığı Gıda ve Kontrol Genel Müdürlüğü 2024). In this study, different potato flour samples produced in Turkey were analyzed for their prosulfocarb concentration due to its high usage.

The objective of this study was to develop an accurate and precise analytical method for the determination of prosulfocarb in potato flour samples. GC-MS system was used to separate the analyte in GC and detect in MS system. After system analytical performance study, the developed method was implemented for the determination of prosulfocarb in the spiked potato flour samples.

2. Materials and Methods

2.1. Chemicals and Reagents

Prosulfocarb (%98) was supplied from Dr Ehrenstorfer GmbH, Germany. Gravimetric standard/sample preparation was followed during all experiments in this study. A 3110.2 mg/kg stock solution was prepared in methanol and diluted to obtain working standard solutions. Methanol was purchased from Merck, Germany. High purity helium gas was attained from a local gas supplier, Türkiye (İstanbul).

2.2. Instrumentation

An Agilent 6890 N gas chromatograph with mass selective detector was used to separate and quantify target analyte. Helium gas was used as mobile phase in GC-MS system at the flow rate of 1.8 mL/min. HP-5MS column (30 m; 250 μm; 0.25 μm) was placed into the oven compartment of GC system. Inlet temperature, injection volume, injection mode were 280 °C, 1.0 μL and splitless mode, respectively. Initial oven temperature was 100 °C. Oven temperature program had only one ramp from 100 °C to 300 °C at the rate of 20 °C/min. MS quadrupole, MS source and transfer line temperature values were 230, 150 and 280 °C, respectively. ChemStation mass spectrum database was utilized to check

and confirm fragments of the analyte obtained by MS system. Qualifier and quantifier ions for prosulfocarb were 128 and 91, respectively.

2.3. Samples

Three different brand potato flours (A, B and C) were purchased from three different sellers located in Türkiye. A clean centrifuge tube was placed into an analytical balance and 50 mg potato flour sample was weighed into the centrifuge tube. The solid sample was spiked to the desired concentration level with the analyte standard solution. The spiked flour sample was diluted to 10 g with methanol in order to extract the analyte from the sample matrix. The sample solution was vortexed for 20 s and centrifuged at 3000 rpm (3461 *g*) for 4.0 min. The upper liquid part was transferred into a clean glass vial and sent to GC-MS system.

3. Results and Discussion

3.1. Analytical Performance of GC-MS System

Two different oven temperature programs were tried to achieve high signal to noise ratio and good chromatographic conditions for prosulfocarb. The programs are given in Table 1. According to the chromatograms given in Figure 1, Program I gave highest signal to noise ratio than Program II. Hence, Program I was selected as optimum oven temperature program for the determination of prosulfocarb by GC-MS system.

Analytical performance of GC-MS system for the analyte was tested by calculating limit of detection (LOD), limit of quantitation (LOQ), linear working range, correlation coefficient (R^2) and percent relative standard deviation (%RSD) values. LOD and LOQ were found by mathematical for-

Table 1. GC-MS conditions for Program I and II.

Parameter	Program I	Program II
Helium flow rate	1.80 mL/min	1.80 mL/min
Inlet temperature	280 °C	280 °C
Injection volume/mode	1.0 µL, splitless	1.0 µL, splitless
Oven temperature program	Initial oven temperature: 100 °C, one ramp from 100 °C to 300 °C at the rate of 20 °C/min.	Initial oven temperature: 100 °C, one ramp from 100 °C to 300 °C at the rate of 30 °C/min.
MS quad/ source/ transfer line temperature	230, 150 and 280 °C	230, 150 and 280 °C

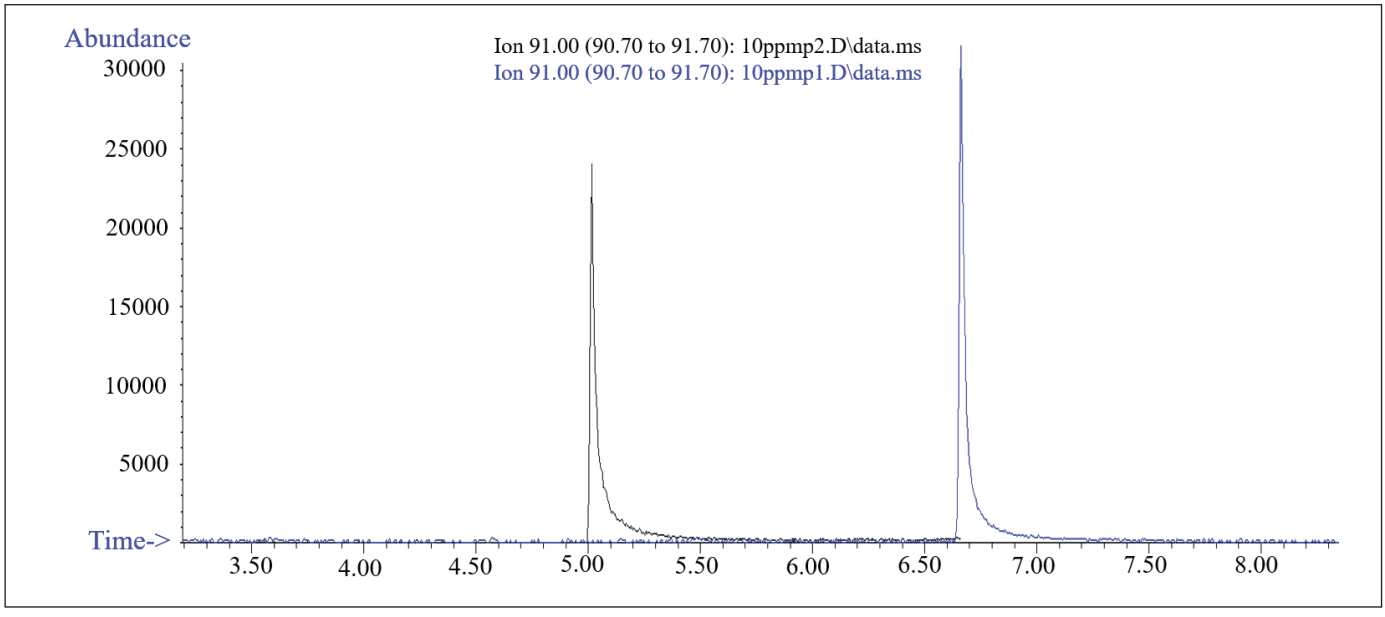

Figure 1. Chromatograms obtained by Program I (blue) and Program II (black).

mulas as 3SD/m and 10SD/m, respectively, where SD is standard deviation of the six repetitive measurements for the lowest concentration in the calibration plot and m is the slope of the calibration plot (Sanagi et al. 2009). LOD and LOQ are two important performance characteristics in method validation. This work compares three methods based on the International Conference on Harmonization and EURACHEM guidelines, namely, signal-to-noise, blank determination, and linear regression, to estimate the LOD and LOQ for volatile organic compounds (VOCs). For this purpose, a series of prosulfocarb standard solutions (2.4-237 mg/kg) was prepared in methanol. Under the optimum GC-MS conditions, all standard solutions were analyzed and calibration plot was drawn between 2.4 and 96.6 mg/kg. Linearity was excellent due to high R^2 value (0.9997). LOD and LOQ values were figured out to be 0.54 mg/kg and 1.80 mg/kg, respectively. %RSD value calculated by dividing standard deviation of six measurements for 2.4 mg/kg to mean of the measurements was found as 7.7%. The analytical performance of GC-MS system is summarized in Table 2. Overlay ion chromatograms belonging to the standard solutions are presented in Figure 2.

3.2. Recovery Studies by Matrix Matching Calibration Strategy

Three different potato flour samples (A, B, C) were treated with the procedure given in Samples Section. Blank analyses for the samples gave no analytical signals for the analyte.

Table 2. Analytical performance parameters for GC-MS system.

Parameter	Value
LOD, mg/kg	0.54
LOQ, mg/kg	1.80
Linear working range, mg/kg	2.4-96.6
R^2	0.9997
%RSD*	7.7
Linear equation	y=84154x+6005

**The %RSD value is belonging to the lowest concentration found in calibration plot.*

For this reason, a calibration plot was drawn using Brand C sample which spiked to six different concentration levels (2.5-99.4 mg/kg). Brand A and Brand B sample were also spiked to different concentration levels and percent recovery results for the spiked Brand A and B samples were calculated using the linear equation (y=100640*x*-37087) obtained by Brand C sample. In addition to matrix matching calibration method, percent recovery values were calculated for Brand A and B samples via external calibration plot with the linear equation as . Table 3 gives all percent recovery and %RSD values for the spiked samples. Overlay ion chromatograms for the spiked samples and standard solution of the analyte are given in Figure 3.

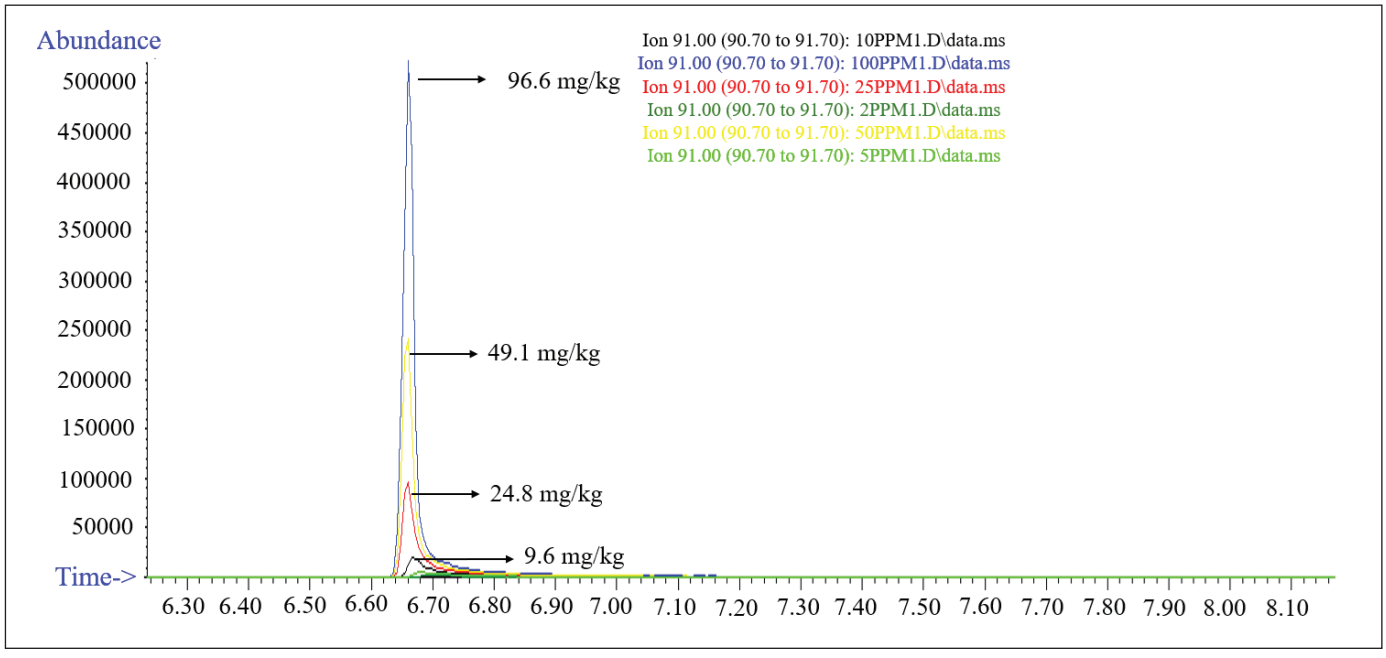

Figure 2. Overlay ion chromatograms (prosulfocarb: 91 m/z) of standard solutions in the range of 2.4-96.6 mg/kg.

According to the results given in Table 3, the developed GC-MS method can be applied to potato flour samples with matrix matching calibration method and external calibration method. High percent recovery results (90.9-105.7%) obtained by matrix matching calibration method validated the applicability and accuracy of the developed analytical method. Low ±SD values (0.5–3.4) also proved the precision of the developed method. When compared to external calibration method, matrix matching calibration strategy gave percent recovery results close to 100% more than external calibration method. Further, positive matrix effects were observed for Brand A (9.9-99.8 mg/kg) and B (10.2-101.7 mg/kg) samples. For these reasons, matrix matching calibration method was appropriate to achieve excellent percent recovery results for the selected sample.

Table 3. Percent recovery results for the spiked potato flour samples.

Sample code	Spiked concentration, mg/kg	%Recovery±SD*	%Recovery±SD**
Brand A	2.6	94.4±1.8	93.3±2.2
	5.0	94.6±3.4	102.9±4.0
	9.9	98.5±2.7	112.6±3.2
	24.9	104.4±1.8	122.8±2.2
	49.9	103.3±0.5	122.5±0.6
	99.8	100.2±0.9	119.3±1.1
Brand B	2.6	92.9±1.7	91.2±2.0
	5.1	90.9±2.1	98.7±2.5
	10.2	99.8±1.7	114.3±2.0
	25.8	105.7±1.8	124.4±2.1
	50.4	100.1±2.5	118.7±3.0
	101.7	97.4±1.5	115.9±1.8

**Matrix matching calibration method. **External calibration method.*

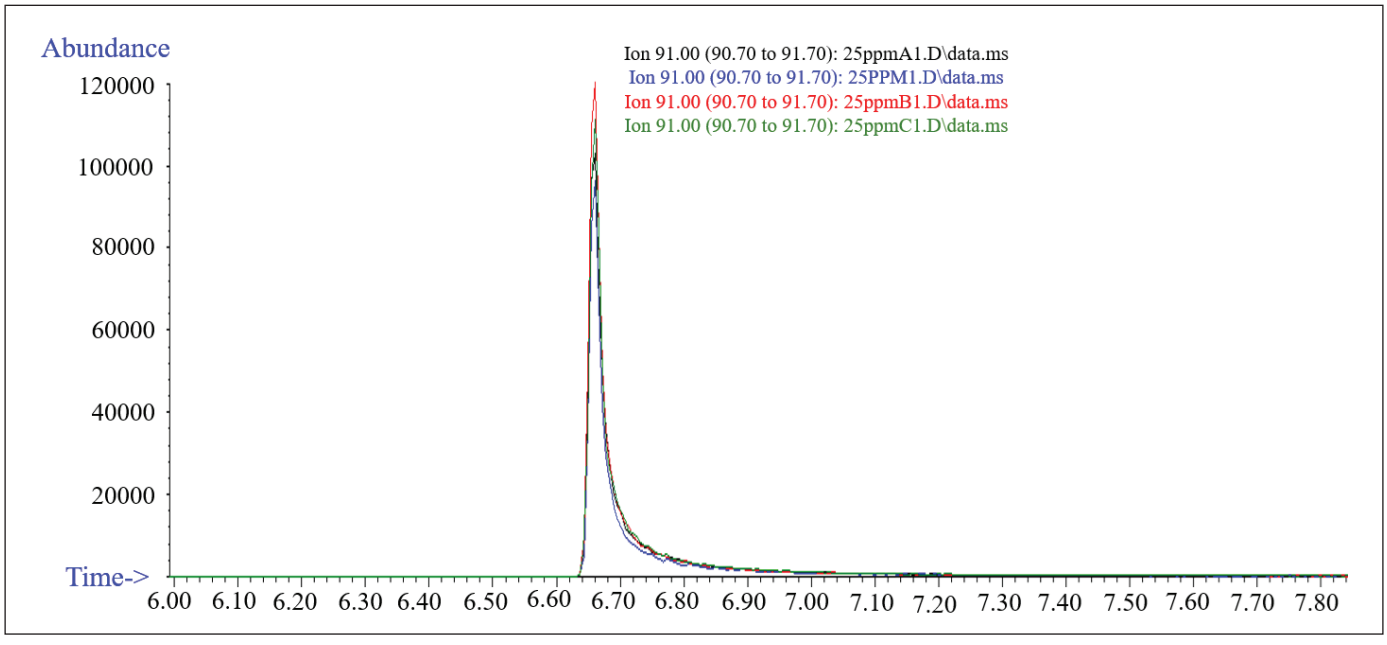

Figure 3. Overlay ion chromatogram for prosulfocarb standard solution (24.8 mg/kg) and spiked potato flour samples (24.9, 25.8 and 25.6 mg/kg spiked Brand A, B and C, respectively).

In literature, there are several analytical methods for the determination of prosulfocarb in vegetables by GC-MS system. For example, Przybylski et al. developed direct analysis method for carbamates. QuEChERS method was used to clean up and extract the analytes from green vegetables. LOD, LOQ and R^2 values were found as 0.50 µg/L, 1.4 µg/L and 0.9772. The method was applied to green bean, spinach, lettuce samples (Przybylski and Bonnet 2009). Another study proposed an analytical method based on QuEChERS and liquid chromatography-tandem mass spectrometry (LC-MS/MS) methods for the determination of pesticides including prosulfocarb in honey. LOQ and R^2 values were 0.01 mg/kg and 0.996, respectively (Gaweł et al. 2019). In 2019, Fu et. al. presented an analytical method for the determination of pesticides in herbal species by gas chromatography-tandem mass spectrometry (GC-MS/MS). QuEChERS method was also used as clean up and extraction step in this study. LOQ and R^2 for prosulfocarb in different herb matrices were 2.0-8.0 ng/mL and 0.9946-0.9992, respectively (Fu et al. 2019). To the best our knowledge, there is no study about the determination of prosulfocarb in potato flour samples in literature. This study proposed an analytical approach for the detection of prosulfocarb in potato flour. In literature, clean up and extraction methods have been generally used to remove the matrix effects and extract the analyte. The developed GC-MS method can be also performed after a clean-up or extraction method. Hence, ppb/ppt detection limits can be obtained for the analyte in potato flour samples.

4. Conclusion and Suggestions

In the presented study, an analytical method for direct determination of prosulfocarb in potato flour by GC-MS system was proposed. Target analyte was separated on HP5MS column within 10 min. After the selection of optimum oven temperature program for the analyte, studies to figure out the system analytical performance were carried out by sending a series of analyte standard solutions to GC-MS system. LOD, LOQ, linear working range, %RSD and R^2 were found as 0.54 mg/kg, 1.80 mg/kg, 2.4-96.6 mg/kg, 7.7% and 0.9997, respectively. Further, applicability/accuracy of the proposed analytical method was checked by spiking potato flour samples. According to the results obtained via matrix matching calibration strategy, excellent percent recovery values (90.9-105.7%) with low SD (0.5–3.4) values verified the applicability and accuracy of the proposed method. The presented method can be used to qualify and quantify prosulfocarb in potato flour samples. This is the first study where an analytical method for the determination of prosulfocarb in potato flour samples by GC-MS system was developed. The developed GC-MS method can be carried out after sample preparation methods like clean up and extraction are performed.

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Author contribution

Sezin Erarpat Bodur: Conceptualization, Formal analysis, Data curation, Methodology, Investigation, Validation, Visualization, Supervision, Writing – original draft, review & editing.

Ethics committee approval: No ethical approval is required.

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