RESEARCH ARTICLE

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Pesticide residues in sauce manufactured from agricultural products

Tarik Balkan[1] • **Kenan Kara**[1]

[1] Department of Plant Protection, Faculty of Agriculture, Tokat Gaziosmanpaşa University, Tokat, Türkiye

Abstract

In this study, pesticide residues in sauce manufactured from agricultural products were examined. A simultaneous multiresidue analysis for 260 pesticides in sauce samples was performed using liquid chromatography with tandem mass spectrometry (LC-MS/MS). The QuEChERS AOAC 2007.01 (quick, easy, cheap, effective, rugged, and safe) was selected as the most suitable protocol for routine determination of pesticide residues. In line with the SANTE/11312/2021 guideline two parameters were used as identification criteria: retention time (RT) with a tolerance of ± 0.1 min in relation to the RT of the analyte in matrix-matched calibration standard and ion ratio tolerance below 30%. The RT deviation in positive samples was always < 0.1 min, and the ion ratio tolerance was < 30%. A total 4 different pesticides were detected in 20 sauce samples. No active ingredient was found in 16 samples. The residue levels were between 10 and 94 µg kg. The residues of acetamiprid, ametoctradin, imazalil sulfate, and metalaxyl-M were below the European Union Maximum Residue Limits (EU-MRLs).

Keywords: Pesticide residue, Processing factor, Sauce, Tomato, LC-MS/MS, QuEChERS

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Correspondence: Tarik Balkan
E-mail: tarik.balkan@gop.edu.tr

INTRODUCTION

Sauce is a French word (sauce) derived from the Latin word salsus, meaning "salty". Sauces are most commonly defined as a food complement and flavor enhancer in gastronomy. Sauce is considered as important as food is in world cuisines. They are mixtures that add additional flavor to the dish, complement the existing flavor and make it easier to swallow. People want to experience the cuisines of different countries thanks to the development of technology, the expansion of the transportation network, international gastronomy tourism and franchise models. Food sauces belonging to French, Indian, Chinese and Italian cuisines enter the lives of people from different countries. In addition, with the spread of fast-food culture, sauces are consumed intensively. The global tomato paste-sauce market has reached approximately 47 million tons by the end of 2020. This figure is expected to increase to 55 million tons in 2025. In Turkey, tomato paste-sauce market is 383 thousand tons in size according to 2020 data (Karaboğa, 2021).

Similar to the other crops, fruits and vegetables used in sauce making have also pest, disease and weed problems. Therefore, pesticides are used to eliminate the negative effects of these pests during growing season and also post-harvest period. Pesticides are any substance or mixture of substances used to protect crops from harmful organisms in order to secure agricultural food production

(EPA, 2022). On the other hand, excessive use of chemicals made without paying attention to the prospectus leave residue on the product. Pesticide residues affect food safety and threaten human health. Residue studies on vegetables such as tomatoes and peppers, which are frequently used in sauce production, reveal the presence of many active substances (Ersoy et al., 2011; Bakırcı et al., 2014; Zengin and Karaca, 2017; Gölge and Kabak, 2015; Polat and Tiryaki, 2018; Balkan and Kara, 2019; Soydan et al., 2021; Balkan and Kara, 2022; Sancar et al., 2022).

Food processing refer to the methods and techniques used to convert raw materials to food for consumption by humans or animals at home or by the food processing industry (Kaushik et al., 2009). These processes are baking, bread making, dairy product manufacture, drying, thermal processing, fermentation, freezing, infusion, juicing, malting, milling, parboiling, peeling juicing and wine making. As a result of the processes which are, pesticide amounts may tend to increase or decrease depending on the physico-chemical properties of the active substance, the nature of the product and the processes they are exposed (Burchat et al. 1998; Cengiz et al., 2007; Kong et al., 2012; Scholz et al., 2017).

The European Food Safety Authority (EFSA) has found that pesticides are higher in unprocessed products, but residues are also found in processed products. However, there are no fixed MRL values for processed vegetables and fruits. For this reason, pesticide residue studies should be carried out in these products. In this study, pesticide residues were investigated in sauces produced from various agricultural products such as tomatoes, peppers and carrots etc.

MATERIALS AND METHODS

Reagents and chemicals

Pesticide reference standards were supplied by Dr. Ehrenstorfer Laboratories GmbH (Augsburg, Germany). Acetonitrile (ACN >99% purity) was supplied by Honeywell (North Carolina, USA). Methanol (MeOH >99% purity), magnesium sulfate anhydrous ($MgSO_4$ >99.5% purity), ammonium formate (NH_4CO_2H >97.5% purity) and acetic acid (AcOH >99% purity) were procured from Merck (Darmstadt, Germany). Water was purified by MP Minipure Dest Up system from Mes (Ankara, Türkiye). The QuEChERS products was purchased from Restek (Bellefonte, USA).

Chromatographic analysis

This study was carried out on LC–MS 8050 model from the Shimadzu®. LC–MS/MS system equipped with UPLC: LC-30AD pump × 2, SIL-20A autosampler, DGU-20A3R degasser, CTO-20ACV column oven and triple quadrupole MS/MS detector. The operating conditions of the device and the gradient program are given in Table 1. All parameters of the instrument were controlled using LabSolution® Insight LCMS software) (Balkan and Yılmaz, 2022).

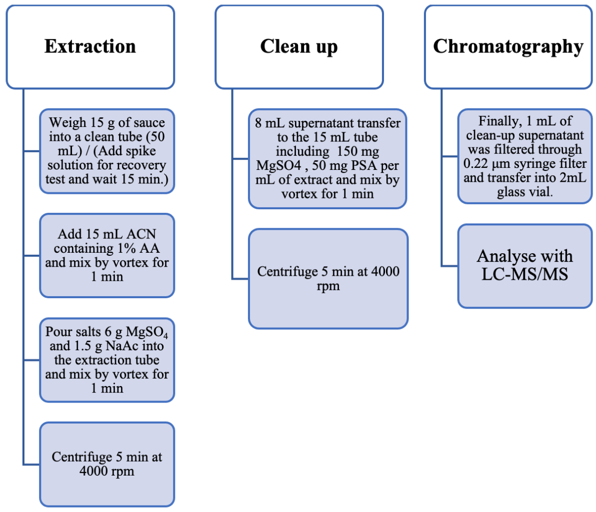

Figure 1. Analytical steps of the QuEChERS-AOAC Official Method 2007.01

Sample extraction and clean up

The official QuEChERS AOAC Method 2007.01 was used for the extraction and clean up procedures (Lehotay, 2007). The followed QuEChERS steps are illustrated in Figure 1. Each of the samples were analyzed in triplicates with LC-MS/MS.

For recovery studies, 15 g of tomato sauce sample were weighed into a 50 ml Falcon tube Then, 150 µl of pesticide mixture was added to 15 g of tube and vortexed for 60 seconds (Polat and Tiryaki, 2019; Dülger and Tiryaki, 2022). It was waited for 15 minutes for the pesticides to interact with the matrix and the steps in Figure 1 were followed.

RESULTS AND DISCUSSION

Two hundred sixty pesticides belonging to different groups (insecticide, acaricide, nematicide fungicide, herbicide, plant grow regulator and some metabolite) were discussed in the study. Analysis of 260 pesticides in sauce samples was performed using LC-MS/MS. In line with the SANTE guideline two parameters were used as identification criteria: retention time (RT) with a tolerance of ± 0.1 min in relation to the RT of the analyte in matrix-matched calibration standard and ion ratio tolerance below 30% (SANTE, 2021; Balkan and Karaağaçlı, 2023). The RT deviation in positive samples was always < 0.1 min, and the ion ratio tolerance was < 30% (Table 1). A total 4 different pesticides were detected in 20 sauce samples. No active ingredient was found in 15 samples. The residue levels were between 10 and 94 µg kg. The residues of acetamiprid, ametoctradin, imazalil sulfate, and metalaxyl-M were found above LOQs (Table 1). The chromatograms and calibration curves of the detected pesticides are given in Figure 2.

The processing factor is defined as the ratio of the pesticide residue level in the processed food to the

Table 1. LOQ, Recovery, Pesticide residue levels and requirements for identification

<table>
<tr><th>Sample</th><th>Pesticides found</th><th>Pesticide residue (mg/kg)</th><th>EU-MRL*</th><th>LOQ (µg/kg)</th><th>Recovery %</th><th>Standart RT (min)</th><th>Sample RT (min)</th><th>Quantification ion / Confirmation ion (m/z)</th><th>Standart ion ratio (%)</th><th>Sample ion ratio (%)</th></tr>
<tr><td rowspan="2">Sauce1</td><td rowspan="2">Acetamiprid</td><td rowspan="2">0.010</td><td rowspan="2">0.5</td><td rowspan="2">3.02</td><td rowspan="2">100.2</td><td rowspan="2">4.896</td><td rowspan="2">4.899</td><td>222.9/ 126.0</td><td>100</td><td>100</td></tr>
<tr><td>223.0/ 56.10</td><td>18.49</td><td>18.68</td></tr>
<tr><td rowspan="2">Sauce2</td><td rowspan="2">Ametoctradin</td><td rowspan="2">0.015</td><td rowspan="2">2</td><td rowspan="2">2.41</td><td rowspan="2">90.3</td><td rowspan="2">8.277</td><td rowspan="2">8.226</td><td>276.1/ 149.15</td><td>100</td><td>100</td></tr>
<tr><td>276.1/ 177.10</td><td>67.83</td><td>62</td></tr>
<tr><td rowspan="2">Sauce3</td><td rowspan="2">Imazalil sulfate</td><td rowspan="2">0.094</td><td rowspan="2">4</td><td rowspan="2">4.67</td><td rowspan="2">88.8</td><td rowspan="2">7.747</td><td rowspan="2">7.753</td><td>296.8/ 159.0</td><td>100</td><td>100</td></tr>
<tr><td>296.8/ 255.0</td><td>32.83</td><td>41.66</td></tr>
<tr><td rowspan="2">Sauce4</td><td rowspan="2">Metalaxyl-M</td><td rowspan="2">0.033</td><td rowspan="4">0.3</td><td rowspan="4">5.29</td><td rowspan="4">106.9</td><td rowspan="4">6.198</td><td rowspan="2">6.150</td><td>280.05/ 220.05</td><td>100</td><td>100</td></tr>
<tr><td>280.05/ 192.05</td><td>60.48</td><td>58.82</td></tr>
<tr><td rowspan="2">Sauce5</td><td rowspan="2">Metalaxyl-M</td><td rowspan="2">0.043</td><td rowspan="2">6.137</td><td>280.05/ 220.05</td><td>100</td><td>100</td></tr>
<tr><td>280.05/ 192.05</td><td>60.48</td><td>66.08</td></tr>
</table>

*EU pesticide database (EC, 2022)

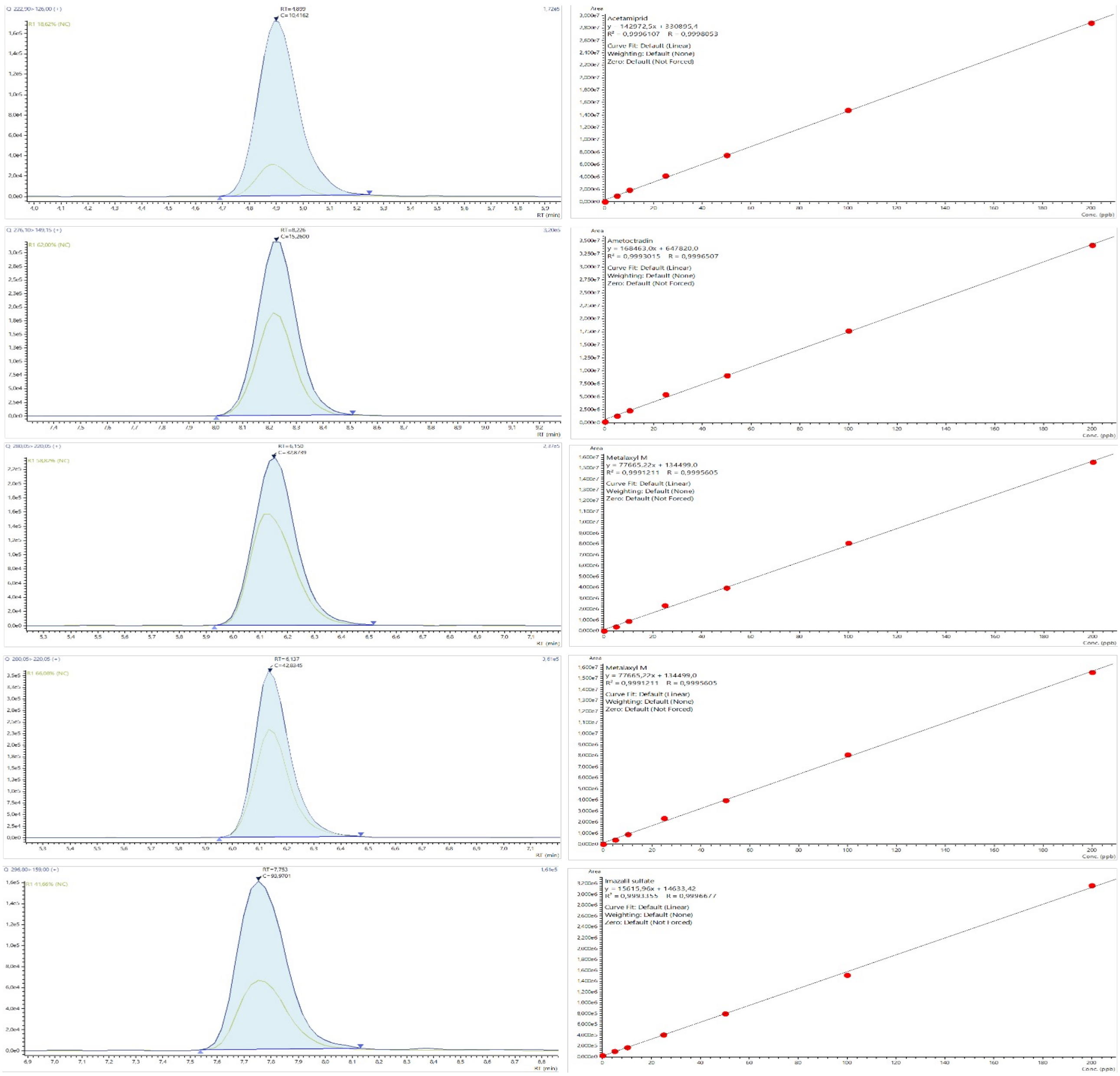

Figure 2. Acetamiprid(a), Ametoctradin(b), Imazalil sulfate(c) and Metalaxy-M (d and e) ion chromatograms for real samples (X axis: Retention time, Y axis: Signal intensity) and calibration curves

pesticide residue level in its raw form (Reddy et al., 2022). The processing factor is necessary to decide whether residues in products comply with legal standards and to assess the risks of residues to human, animal and environmental health in processed products (Scholz et al., 2017; Acoğlu et al., 2018). While determining the MRLs of the new processed products, processing factors are used according to international methods. The determined processing factors are published on the official website of the Ministry of Agriculture and Forestry. In the study, the raw results were evaluated because the residual changes of the product and active substances without processing factor could not be calculated (Görmez, 2019).

Frank et al. (1991) analyzed pesticides on tomato products, including hot pepper, ketchup, juice, tomato paste, and sauce, and found no detectable residue. Fukui et al. (2013) analyzed seventy-four processed food samples from markets in Japan and found pesticide residues above the maximum residue limit in 2 samples. Song et al. (2019) found residues of difenoconazole, dimethomorph, and tebuconazole below established MRLs of China in 10 chili sauce samples collected from local markets in Beijing. Tarifa et al. (2020) found pesticide presence above LOQ in 53% of 103 processed fruit products. In this study, the detected pesticides were below the EU-MRL values (Table 1). The pesticide residues were recorded in 4 tomato samples. The active substances were acetamiprid which were used for tobacco whitefly (*Bemisia tabaci*) and Greenhouse whitefly (*Trialeurodes vaporariorum*) in tomato, ametoctradin against soil-borne pathogens (*Pythium* sp., *Rhizoctonia* sp., *Fusarium* spp., *Verticillium* spp.,) and Downy mildew (*Phytophthora infestans*), metalaxyl-M, against seedling root rot (Collapse) (*Rhizoctonia solani*, *Fusarium solani*, *Pythium* spp., *Oxysporum* spp.), root rot (*Fusarium oxysporum*) and Downy mildew (*Phytophthora infestans*). It is thought that the residue in the sauce, in which the active ingredient of imazalil sulfate was detected, was caused by the orange juice in its content. Imazalil sulfate is a licensed fungicide against storage rot (Green mold rot) (*Penicillium digitatum*) and blue mold rot (*Penicillium italicum*) on oranges.

CONCLUSION

In this study, 4 pesticides were detected in 20 sauce samples. No active ingredient was found in 15 samples. The residue levels were between 10 and 94 µg kg. The residues of acetamiprid, ametoctradin, imazalil sulfate, and metalaxyl-M were found above LOQs. No pesticide residues were detected in onion sauce, chickpea sauce, pea sauce, eggplant sauce, red bean sauce, green lentil sauce, acuka, red beetroot, peach jam, hot sauce, carrot hot sauce, hot sweet sauce, red beet hot sauce, purple cabbage sauce, tomato puree. The results obtained from this study show that pesticide residues should be monitoring in processed agricultural products.

COMPLIANCE WITH ETHICAL STANDARDS

Conflict of interest

The authors declared that for this research article, they have no actual, potential or perceived conflict of interest.

Author contribution

The contribution of the authors to the present study is equal. All the authors read and approved the final manuscript. All the authors verify that the Text, Figures, and Tables are original and that they have not been published before.

Ethical approval

Ethics committee approval is not required.

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Data availability

Not applicable.

Consent for publication

Not applicable.

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