Food safety aspects of post-harvest fungicides used on citrus fruits

Anna Buzás and Katalin Lányi*

University of Veterinary Medicine Department of Food Hygiene,

István u. 2. H-1078 Budapest, Hungary

**e-mail: lanyi.katalin@univet.hu*

Abstract

The storage of fruits can be made safer by using fungicides that inhibit the development of moulds during transportation. Nice-looking fruits with longer shelf-life are basic consumer expectations, however, it is even more important that moulds may produce mycotoxins posing serious risk to human health. The most commonly used fungicides for this purpose are imazalil, thiabendazole, and prochloraz. The consumer awareness of these fungicides was surveyed by means of an electronic questionnaire. An LC-MS / MS method was developed and validated for measuring imazalil, thiabendazole, and prochloraz in various fruits. Various commercially available fruits were examined for these three compounds, and the effectiveness of the most popular fruit cleaning methods for removing these three compounds from the surface of fruits was also tested based on the results of the questionnaire. Imazalil was found also in products labelled as organic: on banana in a higher content, while on lemon and orange in a lower one, however these values were far below the MRLs for adults. Our experiments investigating the effectiveness of peel cleaning procedures showed that neither the cleaning was complete, nor the chemical efficacy of a cleaning method was in proportional to its popularity.

Keywords: post-harvest fungicides, citrus fruits, surface treatment

Introduction

Synthetic pesticides have been helping the development of food production since the 1940s. The production of worldwide used pesticides is growing continuously, around 11% annually. Between the 1950s and 2000, it rose from 0.2 million tonnes to over 5 million tonnes (Ramady et al., 2015).

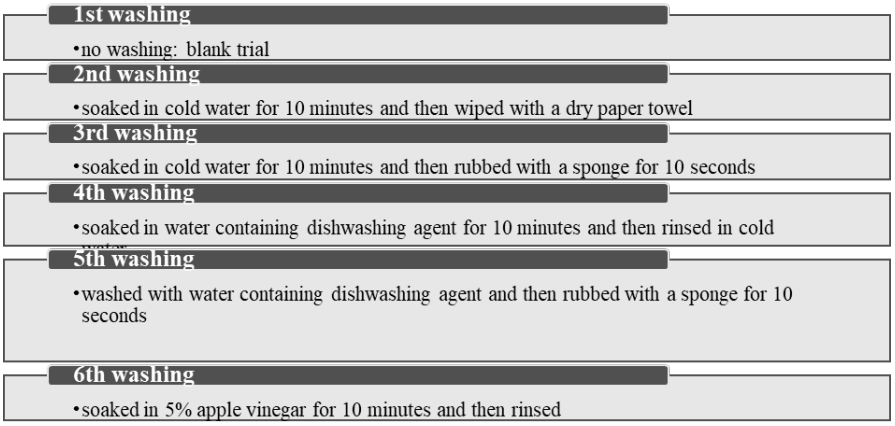
Nowadays organic farming methods are becoming more and more prevalent, however many fruits still require the use of pesticides. The surface treatment of citrus fruits after harvest is necessary to prevent damages caused by the phytotoxins of plant pathogenic fungi. Though, we can reduce pesticide residues during food processing and in kitchen use by means of washing, peeling, canning or cooking (Kellermann et al., 2018).

Many different post-harvest treatments are used. The usual treatment of citrus fruits can be done by soaking in or spraying with fungicides including thiabendazole, o-phenylphenol, propiconazole and imazalil (Vass et al., 2015), or through the immersion into water emulsion wax containing fungicides (primarily imazalil, thiabendazole and prochloraz). These methods are used in many places to prevent moisture loss during storage, transport and distribution. Their use is more significant in international markets. For example, about 28% of the world's lemons is produced in Argentina, and Tucumán itself produces 90% of those fruits. As this production area is 10 000 to 17 000 km far from overseas markets, fresh fruits take 25 to 40 days to reach the final consumer; this journey time affects the global competitiveness (Sepulveda et al., 2015).

Material and method

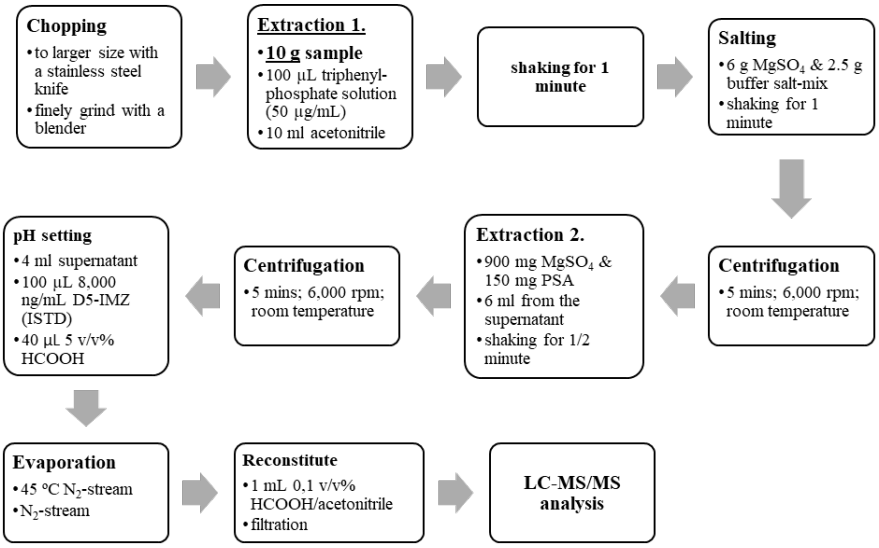
Questionnaire*:* Our study was based on an online questionnaire created in Google Forms. The questionnaire contained 34 questions constituting several parts. The first part was about demographic data. It is followed by questions on the fruit purchasing and utilization habits as well as about the treatment agents. The last part deals with washing methods, and at the end of the questionnaire the respondents were requested to give their own ideas.

Laboratory study: For the laboratory experiments commercially available mandarin and lemon were bought and treated differently in six bowls (see figure 1.). The fruits' peel was declared unfit for human consumption by the dealer.



1. Figure. Setup of the cleaning trials

Sample preparation: For sample preparation the so-called QuEChERS method was used and adapted to suit our needs. (Vass, 2017) (see figure 2.)



2. Figure. The sample preparation process

LC-MS/MS measurements: The fungicide content of the extracted samples was measured by UHPLC-MS / MS with a Shimadzu LCMS-8030Plus system.

Data processing: The answers of the questionnaire were collected and processed as well as the different data were compared by Microsoft Excel,. LC-MS / MS results were processed using SHIMADZU LabSolutions®.

Results and discussion

Results of the questionnaire: The questionnaire was completed by 282 respondents over almost 3 months, showing a fairly homogeneous demographics, mainly young women. Exactly 80.4% were women and 19.6% men, 60.5% 18-25 years old, 20.3% 26-35 years old. Most fruits are bought in hypermarkets, supermarkets, usually a few times a week, but some shop several times a week (14 respondents). Most of the respondents (153 people) use citrus peel and grate it, for example to cakes and cookies. However, 199 respondents do not buy any individually packaged citrus zest, peel or rind, thus unless they buy "organic" fruit, they use pesticide treated fruit. There are various sources of exposure in addition to cakes, for example, we often find circled citrus fruits in drinks, and many people put fruits in salads. According to the answers, there are respondents using lemon to make lemon syrup, which can be a process that can enrich the minimal quantity of residues. 95.5% of those who completed the questionnaire has already heard of these substances, but this information comes from the family or acquaintances generally and not from a professional source. The answers to the questionnaire revealed that many respondents - 40.21% of those who purchase fruit - do not pay attention to whether the product is surface-treated, because they do not even know where to look for these signs.

Laboratory test results:

Test measurements:

For imazalil the result was extremely high on 1 banana and 1 mandarin peel, exceeding MRL that is 2 mg/kg for bananas and 5 mg/kg for mandarins. In the other samples very low values, much lower than MRLs, were measured. Despite our low detection limit, most samples was not detectable for prochloraz, as well as very low levels of thiabendazole. Most samples showed detectable but no measurable levels.

Wash-off Trials:

From among the results of lemon wash-off experiments, only trial 4 was significant from the aspect of imazalil compared with the control. However, there is some reduction in each sample, which may be "effective" or "ineffective" relative to one another. None of the washing methods can remove all pesticides. In the case of mandarin, three from the five washing methods gave significant results with respect to imazalil (trials 1, 3 and 5, i.e., soaking in cold water,

dishwashing water and apple vinegar respectively). In the case of prochloraz, none of the washes caused a significant cleaning of lemon. In the case of mandarin, prochloraz was not detected either in the control fruit or in the sample obtained from the washed fruits. Thiabendazole could be reduced in lemon significantly by trial 4, i.e., washing in detergent water for 10 seconds and rubbing with a sponge. For mandarin, thiabendazole was also adequately reduced by a smooth cold water wash. Considering the results for citrus zest, peel or rind use it is worth buying 'organic fruit', but if this is not feasible, clean the fruit surface well. Rinse them with cold or dishwashing water, wash with a sponge, and then wipe with a paper towel. However, the best is to soak the fruits in apple vinegar.

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