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Determination of Pesticide Residues in "Organic" Wines on the Swiss Market

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Introduction

"In vino veritas" says an old proverb. The aim of this study was to search for the truth in "organic" wines available on the Swiss market. As the European (and Swiss) maximum residue limits (MRL) for pesticides in wine are fairly high compared to the concentrations usually found in conventionally produced wines, there is normally no need for a particularly sensitive method of analysis. With the gas chromatographic (GC) methods currently used in pesticide analytical laboratories detection limits in the region of 0.01 mg/kg are reached, allowing to judge whether the concentration of a residue is above or below the maximum residue limit (MRL).

In this study the median values of the concentrations of eight frequently encountered pesticides in 15 conventionally produced wines analysed were all below 0.01 mg/kg. This observation is in good accordance with data found in the literature (1–4). Pesticide concentrations in grapes are greatly reduced during vinification. They remain in the grape-skins or are degraded during fermentation and storage (3, 4). Thus, methods with a detection limit of 0.01 mg/kg are not suitable for comparing residue concentrations in conventional and organic wines, with a view to checking authenticity of the latter.

By applying a simple extraction of the wine with hexane with subsequent concentration and GC-MS analysis, we found that it is easy to reach a detection limit of 0.0005 mg/kg. With this novel method 83 samples of "organic" wines were analysed for 82 different pesticides. The results gave rise to several questions concerning the term "organic".

Experimental

Samples

83 samples of "organic" wines and 15 samples from conventional production were taken. The samples were of miscellaneous origins and were taken officially on the Swiss market in a co-ordinated action together with the official food control authorities of the cantons Aargau and Zürich. Analysis was commenced immediately after opening the bottles. The remaining samples were then stored in a refrigerator at 5°C. Pesticide concentrations remained stable under these conditions for at least one week.

Analytical method

Reagents and material

- Sodium chloride purum Fluka 71381
- n-Hexane für die organische Spurenanalyse Merck 1.04371
- Isooctane für die organische Spurenanalyse Merck 1.15440
- 2-Propanol z.A. Merck 109634
- Sodium sulfate anhydrous z.A. Merck 1.06649.0500
- 1, 11-Dibromoundecane purum Fluka 34410 (internal standard)
- n-Hexane containing 1 mg/l 1,11-dibromoundecane
- GC-MS system. In this study a Fisons MD800 was used with EI ionisation in the full scan mode. Column DB-5 MS l = 30 m, ID = 0.25 mm, film 0.5 µm (J&W # 122-5536)
  Carrier gas helium 75 kPa
  Injection 5 µl in 2 seconds (splitless mode, splitless liner ID = 3 mm, splitless time 1 min), injector temperature 200°C
  Temperature programme: 1 min at 115°C, heat with 30°C/min to 180°C, heat with 3°C/min to 280°C, keep at 280°C for 7 min
- Ultrasonic bath
- Rotary evaporator Büchi Rotavapor RE120
- Sprayer (aerosol propellant for 2-propanol)
- Cylindrical glass vessels 80 ml approx. ID = 3.5 cm approx. (e.g. centrifuge tubes) with ground-glass stopper or screw cap (teflon or aluminium foil seal)
- 10 ml conical flask prepared as follows: Pipet 0.20 ml of isooctane into the flask and measure the height of the liquid surface above the bottom of the flask (h_1). Add another 0.10 ml of isooctane and measure the height again (h_2).

All reagents and materials shall be tested for contamination by performing blank analyses regularly.

Procedure

1. Weigh 50.0 g of wine sample into a cylindrical glass vessel.
2. Add 10 g of sodium chloride.
3. Add 5 ml of hexane containing 1mg/l 1,11-dibromoundecane.
4. Close the vessel and shake vigorously for 1 minute.
5. Treat in an ultrasonic bath until the hexane separates as a white, emulsified layer on the surface.
6. Spray a small amount of 2-propanol onto the hexane layer and wait for the emulsion to decompose sufficiently to allow the withdrawal of at least 2 ml of clear hexane phase.
7. Transfer as much as possible of the hexane phase into a 5 ml vial with a Pasteur pipette and dry by adding sodium sulfate and shaking.
8. Transfer as much as possible of the dry extract by decanting into a 10 ml conical flask.
9. Add 0.5 ml of isooctane.
10. Concentrate by means of a rotary evaporator (T = 20–30°C, vacuum) to a volume of 0.25 ± 0.05 ml (the height of the liquid surface above the bottom of the flask should be between h_1 an h_2). If the height is less than h_1 (corresponding to a volume of less than 0.2 ml), discard the extract and start the analysis from the beginning.
11. Analyse the concentrated extract by GC-MS (conditions see under "reagents and material").
12. Calibrate the system by proceeding to steps 8 to 11 with known concentrations c_i (mg/l) of pesticides in hexane containing the internal standard.
13. Calculate the pesticide concentrations c_s (mg/kg) in the sample by means of the following equation: $c_s = c_i * 0.1$ (the dimension of the proportionality factor is l/kg).

Quality control

All positive samples were analysed at least in duplicate. Employing the MS-detector always in full scan mode enabled the analyst to confirm the identity of the peaks by spectrum fit in addition to the calibrated retention times. In all four blanks no trace of any pesticide was detectable. Recovery values at spiked concentration levels of 0.01 mg/l were 92 % for cyprodinil, 99 % for fludioxonil, 91 % for pyrimethanil, 89 % for diethofencarb, 106 % for procymidon, 85 % for vinclozolin, 40 % for metalaxyl, and 90 % for iprodion. The results of four wine samples were in a good accordance with those found in the cantonal laboratory Schaffhausen.

Results

All samples were tested for 82 different pesticides. Residues of eight different pesticides were found in 51 (61 %) of the 83 analysed "organic" samples and in 13 (87 %) of the 15 conventional samples. Table 1 shows the identity, the frequency

Table

Frequency, median, maximum concentration and MRL values for the individual pesticides

	Cyprodinil	*Fludioxonil*	*Pyrimethanil*	*Diethofencarb*	*Procymidon*	*Vinclozolin*	*Metalaxyl*	*Iprodion*
Conventional samples								
Frequency	7	7	7	4	2	0	4	7
Median	0.043	0.018	0.0028	0.0015	0.0057	< 0.0005	0.0015	0.0018
Maximum	0.120	0.031	0.013	0.0039	0.0079	< 0.0005	0.010	0.015
«organic» samples								
Frequency	36	22	13	2	7	1	5	13
Median	0.0016	0.0016	0.0007	0.0022	0.0007	0.001	0.0015	0.0013
Maximum	0.059	0.014	0.015	0.0035	0.0014	0.0010	0.0023	0.0052
MRL (Switzerland)	0.5	0.5	1	0.5	2	1	0.6	2

The median values refer only to the samples in which the concerned pesticides were found.
All concentrations are in mg/kg. The MRL values are tolerance values.

of detection, the median, and the maximum concentration as well as the MRL values for the individual pesticides.

Discussion

The results give rise to a number of questions:

– *Where do the residues come from?*

There are several possible explanations:

– Pesticide application on the vines.

– Contamination from pesticide application in the neighbourhood of the vines.

– Contamination from residues in soil formerly contaminated with pesticides.

– Contamination from wine press or other equipment used for both organic and conventional wine production.

– Blending of conventional wine with organic wine.

The producers of the positive samples were asked to explain the residues in their products. Among the answers the most frequent one was contamination from pesticide application in the neighbourhood of the vines.

– *May a wine containing pesticide residues be called "organic"?*

– *If yes, which pesticides and how much of these are admissible, and on which way may they have come into the wine?*

– *May an organic wine be treated with sulfur dioxide? In the Swiss legislation (6) the answer is "yes".*

– *May an organic wine be produced in a polluted environment (soil, air and water contamination)?*

– *Does it matter if large amounts of (permitted) copper fungicides are used in the production of organic wine where it is well known that copper is not degraded in soils, leading to a long term infertility of the soil?*

It will be a (difficult) task for the legislator to set criteria for organic wines in order to allow enforcement of food legislation in accordance with consumer expectations.

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Summary

A new method for the determination of pesticide residues in wine is presented. The method is simple and sensitive. The wine sample is extracted with hexane, the extract concentrated and analysed by GC-MS. 83 "organic" and 15 conventional wine samples were analysed. Residues of either cyprodinil, fludioxonil, iprodion, pyrimethanil, procymidon, metalaxyl, diethofencarb, or vinclozolin were found in 61 % of the "organic" and in 87 % of the conventional wines. The origin of the residues and consumer's expectations from organic wines are discussed.

Zusammenfassung

Es wird eine neue, einfache und empfindliche Bestimmungsmethode für Pestizidrückstände in Wein vorgestellt. Die Weinprobe wird mit Hexan extrahiert und nach Aufkonzentrieren mit GC-MS analysiert. 83 biologische und 15 konventionell produzierte Weinproben wurden analysiert. Rückstände von Cyprodinil, Fludioxonil, Iprodion, Pyrimethanil, Procymidon, Metalaxyl, Diethofencarb oder Vinclozolin wurden in 61 % der biologischen und in 87 % der konventionellen Weine gefunden. Die Herkunft der Rückstände und die Konsumentenerwartungen werden diskutiert.

Résumé

Une nouvelle méthode de dosage des pesticides dans le vin est présentée. La méthode est simple et sensible. L'échantillon est extrait à l'hexane, concentré et analysé par GC-MS. 83 vins biologiques et 15 vins de production conventionnelle ont été analysés. Des résidus de cyprodinil, fludioxonil, iprodione, pyrimethanil, procymidone, metalaxyl, diethofencarb ou de vinclozoline ont été trouvé dans 61 % des échantillons biologiques et dans 87 % des échantillons conventionnels. L'origine des résidus ainsi que les attentes des consommateurs sont discutés.

Key words

Pesticides, Wine, Organic production, Analysis, Method

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