

# **relana<sup>®</sup>-Method-Ringtest**

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**Pesticides on Leaves**

**Part 2: Apple Leaves**

**(Part 1: Vine Leaves)**

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# 1 Introduction

The analysis of leaves for pesticide residues in/on several fruit crops like apples, pears or grapes is often part of monitoring projects in order to verify good agriculture practice related to the specific requirements of the particular rules (f. ex. integrated cultivation, national or regional quality labels etc.).

Within the 2016 working programme of the laboratory quality circle relana® this topic is on the agenda in order to get a first overview about the laboratory performances and the comparability of pesticide residue analyses of such leave samples after common treatments with pesticide formulations.

## 2 Test material

In order to provide appropriate test material, it was agreed to use leaves, which were treated by the growers in a common way during the current season. Vine leaves and apple leaves were identified as appropriate test materials for the method ring test, because these types of leaves are the most important ones analysed by the laboratories. This report is related to the analysis of apple leaves (Part 2), while a separate report deals with the results of the vine leaves (Part 1).

The leaves were picked at an apple plantation near to Hamburg. The plantation is part of a fruit research institute, where most of the apple and pear growers of the local region are organised and get advice from. The variety of the apples is "Red Jonaprince", planted in 2011. The field is partly covered by hail nets.

The leaves were taken from so called "long sprouts", which are located between 0,8 and 1,8 m above the ground. From each sprout 4 – 5 leaves were taken. The trees were selected by field line 12 and 13; tree side south resp. north and hail net "yes" resp. "no". The leaves were picked the 25. July 2016 and they were directly transferred to the office of Lach & Bruns. The total leaves (ca. 10 kg) were mixed thoroughly and divided into 11 portions of ca. 350 g each by Lach & Bruns.

The samples were send out to the relana® laboratories the 26. July 2016. To keep the leaves at appropriate condition, the (already frozen) samples were packed and sent using dry ice.

## 3 Results and Discussion

The samples were sent to the laboratories including an order sheet asking for the analysis of current pesticides. As the apple leaves contain incurred residues only, the evaluation of the results is done using the comparability criterion (z-score model). Every lab is given an individual lab code.

All in all, the laboratories reported 17 different pesticides with significant levels above the common reporting limit (RL) of 0,01 mg/kg, including copper (Cu) and the metabolites Phthalimid (Folpet) and THPI (Captan).

The institute forwarded the application list (Pesticide formulation and active substances), which have been used for the treatment of this apple field. First application was performed on 24. March 2016 (Copper-hydroxide), the latest on 14. July 2016 (Captan).

All in all, 14 different applications were performed during the current season, including copper-hydroxide and sulphur. After the exclusion of sulphur (which was not asked to be analysed for), 13 active substances are still left, which should have been possible to detect on the leaves:

Boscalid, Captan, Chlorantraniliprol, Dithianon, Fluopyram, Imidacloprid, Myclobutanil, Penconazole, Pyraclostrobin, Spirodiclofen, Tebuconazole, Copper and Pirimicarb.

Five laboratories detected Pirimicarb in traces only (< RL). The other 7 labs did not report a Pirimicarb result at all. Having taken a look on the application map, Pirimicarb was applied just once at 2. May 2016 with 0,25 kg/ha. All other pesticides have been used - for the last application - later: Middle of May, in June or in July. Apparently, the concentration of Pirimicarb on the leaves has decreased to a level below the common RL of 0,01 mg/kg.

Additional, the labs reported some more pesticides resp. metabolites:

- Dodine (assigned value 0,030 mg/kg; reported by 10 labs),
- Folpet (a.v. 0,28 mg/kg; reported by 7 labs),
- Dithiocarbamates expr. as CS<sub>2</sub> (a.v. 0,20 mg/kg; reported by 8 labs),
- Phthalimid (PI) as a possible metabolite of Folpet (4 labs),
- THPI as a metabolite of Captan (6 labs).

### *Discussion of the results related to the particular pesticides*

#### **A) Pesticides showing a typical distribution of the results (10 pesticides and Copper)**

The results related to

*Boscalid, Chlorantraniliprol, Dodine, Fluopyram, Imidacloprid, Myclobutanil, Penconazole, Pyraclostrobin, Spirodiclofen, Tebuconazole, and Copper*

are well comparable with typical result distributions (bell-shaped-curve, Gaussian curve).

Related to these pesticides, only some very few significant outliers are observed: Boscalid, Dodine, and Pyraclostrobin.

Three labs did not analyse for Dithiocarbamates and also three labs did not analyse for copper.

**Related to the pesticides and copper mentioned above, the results of the relana<sup>®</sup> laboratories are close together showing a homogenous distribution. This is a very satisfying situation, indicating the competence of the laboratories to analyse apple leaves and providing reliable results.**

## **B) Pesticides showing an atypical distribution of the results (4 pesticides)**

### Captan

The results of Captan show **three** significant **clusters** of results:

- Four labs reported levels between 202 mg/kg and 259 mg/kg, which is a very homogenous distribution.
- Four labs reported levels between 110 mg/kg and 158 mg/kg, which is also a very homogenous distribution.
- Three labs reported levels of 20 mg/kg resp. 44,5 mg/kg resp. 47 mg/kg, which are much lower compared to the other laboratories.

This is a situation, which cannot be explained at the moment. The results reported for THPI give no additional hints to explain this phenomenon.

### Dithianon

The results of Dithianon differ significantly from each other, covering a concentration range from 0,068 mg/kg to 21 mg/kg! Homogenous clusters of results cannot be identified. The robust standard deviation is 7,49 - strongly exceeding the target standard deviation acc. to Horwitz, which is 1,31. Once again these results confirm, that the analysis of Dithianon needs special requirements and special care, which cannot be provided by a multi method approach.

### Folpet

The results of the 7 labs, which reported levels of Folpet do not differ significantly from each other and show a typical distribution. Four labs did not report Folpet, even though the assigned value is at 0,28 mg/kg.

### Dithiocarbamates

The results of seven out of eight labs, which reported levels of Dithiocarbamates are within a range between 0,11 mg/kg and 0,29 mg/kg, which is satisfying considering the instability of Dithiocarbamates. One Lab reported a level of < 0,05 mg/kg (RL), which is clearly below the other results (assigned value: 0,20 mg/kg). Three labs did not analyse for Dithiocarbamates and therefore did not report results.

## **Conclusion**

**All in all, the participating laboratories present very satisfying performances of pesticide residue analyses in/on apple leaves. The described deviations related to particular pesticides will be discussed and questioned individually with the particular laboratories. Once again it is confirmed, that the analysis of Captan and of Dithianon is demanding and challenging, independent of the matrix. This will be followed up by relana® in the near future.**