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Interpretation aid in the use of the BNN orientation value for pesticides

1) Detection of metabolites

Metabolites (decomposition or breakdown products) of pesticides are also occasionally detected in organic products. The residue definition under the EU Regulation 396/2005 is ruling for an assessment according to the BNN orientation value. This means that the detection of a pesticide and its metabolite(s) is generally considered as evidence of the presence of the active ingredient and the sum of the metabolites is used to assess the level of the finding.

In individual cases, it may be useful to deviate from this rule because the BNN orientation value has a different objective from the legal MRLs and / or individual residue definitions are technically questionable. This may mean disregarding the BNN orientation value if the assessment of the is most likely due not to the parent compound but to environmental or process contamination (see for example 2) phthalidimide detection). In other cases, it may be useful to assess the metabolite individually if, as in the case of phosphonic acid (see fact sheet phosphonic acid), which although a pesticide active ingredient, is in the great majority of cases not due to the potential parent material (in this case fosetyl).

A case-by-case assessment of whether the metabolite should not be taken into account because it may have other parent substances / sources not associated with pesticide use is particularly recommended if the parent substance itself cannot be detected.

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2) Phthalimid detection in organic products

From August 26th 2016 a new residue definition of the fungicide Folpet shall apply, including in addition to Folpet also the metabolite Phthalimid (“Folpet: Sum of Folpet and Phthalimid, expressed as Folpet, Regulation (EU) 2016/156). Moreover, Phthalimid is also a metabolite of the insecticide Phosmet (see EFSA reasoned opinion), but nevertheless not included in its residue definition.

As the laboratory circle relana® has shown on the basis of several hundred analysis results via correlations and practical experience of the laboratories and based on a hypothesis developed by Labor Friedle, Phthalimid is produced in many cases without the presence of Folpet or Phosmet. Phthalimid is formed by the ubiquitous chemicals „phthalic acid“ and „phthalic anhydride“ in reaction with primary amino-groups, which are usually part of the food matrix. This happens especially under heating conditions, so that dried products are particularly affected (relana® 2016). Phthalic anhydride is used f.ex. in resins, paintings and newspaper printings and is detected in nearly every (house) dust sample.

Thus Phthalimid is predominantly not a metabolite of Folpet – contrary to the new residue definition – and therefore does not indicate its application. BNN guideline value for

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Folpet/Phosmet/Phthalimid is only applicable, when in addition to Phthalimid also Folpet or Phosmet are detected.

Furthermore, above mentioned information shall be taken into consideration on a case-by-case basis if Folpet or Phosmet are detected as well, because it is not plausible that the entire amount of Phthalimid is derived by the metabolism of Folpet or Phosmet only.

Literature

relana (2016): POSITION PAPER No. 16 -03 "Phthalimid: Metabolite of Folpet or unavoidable Artefact ?" Version 2016/07/22
http://www.relana-online.de/wp-content/uploads/2016/07/PP_16-03_Folpet-PI_vers20160722.pdf

Commission Regulation (EU) 2016/156 of 18 January 2016 amending Annexes II and III to Regulation (EC) No 396/2005 of the European Parliament and of the Council as regards maximum residue levels for boscalid, clothianidin, thiamethoxam, folpet and tolclofos-methyl in or on certain products (Text with EEA relevance)
http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32016R0156&qid=1469718309915&from=EN

Reasoned opinion on the modification of the existing MRLs for phosmet in citrus fruits, pome fruits and rape seed (EFSA Journal: EFSA Journal 2013;11(12):3510 [33 pp.])
http://onlinelibrary.wiley.com/doi/10.2903/j.efsa.2013.3510/epdf

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3) Dithiocarbamate detection in organic products

Dithiocarbamate is the generic term of a group of pesticides, which contain a carbon-sulphur (CS2) bond in their molecular structure. The fungicides Mancozeb, Maneb, Metiram, Propineb, Thiram and Ziram belong to this group. Dithiocarbamates are not permitted in organic agriculture.

Dithiocarbamates are determined indirectly as a total of the CS2 bonds found in the sample. This means that as a rule the individual substances cannot be determined.

In addition the analysis is affected when the plant contains natural sulphur or carbon-sulphur bonds, which may lead to false positive results. This is known to be the case for example with Brassicaceae-family (e.g. cabbage species, rape) and the Allium genus (onions and garlic). There are further specific anomalies that can occur in individual crops, which may also lead to false positive results. It is known that ripe papaya fruit which can produce carbon-sulphur as a result of strong enzyme activity (BUT it is also known that dithiocarbamates are applied in papaya production).

The information above is to be taken into consideration in a case by case assessment of analytical results showing the presence of dithiocarbamates in organic products.

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Naturkost Naturwaren

4) Bromide detection in organic products

Plants take up bromide from the soil. It is not possible to determine analytically if the bromide is from a natural or an anthropogenic source.

Methyl bromide is used for soil sterilisation. The gas can be detected only in the short term (half life in the soil is about 10-30 days). The residue is bromide, which does not decompose and is therefore found in the soil years after exposure to the gas. In such cases bromide should have already been detected in previous samples from the same area, and conventional usage would have been proven.

Bromide can also be from natural sources; this is particularly the case with former seabeds and land in close proximity to the ocean. To estimate this, the geographical location and the bromide/chloride-ratio can be utilized. If the bromide value is caused by sea salt, then normally the chloride value is also increased. In such cases the chloride value should be at least 50 times the bromide value, as a rough estimation. Unfortunately until now there is no reliable data for accurately determining limits for the bromide/chloride-ratio.

Furthermore, methyl bromide is used as a gas in (shipping) containers and as post harvest agent for dried fruit for instance. Therefore calculating back to the fresh product is generally not appropriate.

If inorganic total bromide higher than 5 mg/kg is detected, the source of the increased bromide value should be investigated and if necessary the competent certification body should be informed.

The food can still be traded when inorganic total bromide is higher than 5 mg/kg, if there is no suspicion of illegal use of methyl bromide.

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