



Pesticides 3.0

*new contaminants and
limitations of analysis*

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New contaminants

- Pesticide ? *Pyrrolizidinalkaloids (PA)*
- Contaminant (processing, environmental) ?
- Ingredient ?
- Technical additive ? *Chlorat*
- Unindenting additive ?
- No idea about source ?



Anthraquinone / PAH

CHLORAT

Main sources of Chlorat

- *Using drinking water, which is legally treated with chlorine containing disinfectants*



Study^{)}: rinsing vegetables with water containing
0,7 mg/l Chlorat (= WHO-guideline value)*

→ 0,08 mg/kg in lettuce resp. 0,03 mg/kg in spring onions

- *Beverage-concentrates made by using local (chlorinated) drinking water*

^{*)} source: Analytica Alimentaria GmbH, Report related to Chlorat, 8.4.2014

Main sources of Chlorat

- *Process water*
- *„Hydro-Cooling“*



*Example: Carrots of origin USA with 0,54 mg/kg Chlorat
after Hydro-Cooling*



CHLORAT

Main sources of Chlorat

- *Fertilizers*
up to around 10 mg/kg Chlorat



- *Levels of Chlorat in Strawberries after fertilisation: up to 0,07 mg/kg *)*



*) source: Analytica Alimentaria GmbH, Report related to Chlorat, 8.4.2014

CHLORAT (AND PERCHLORAT)

Analytical approach:

- *Single Residue Method*
resp. specific Multi-Method!



„POLAR“ QUECHERS-METHOD (QuPPe)

covers f.ex. Chlorat, Perchlorat, Phosphonic acid, etc.

But:

*Different analytical modules have to be applied
depending on the molecules to be analysed!*



CHLORAT (AND PERCHLORAT)

Facing analytical quality.

proof:acs

Ring Test
„Chlorate and Perchlorate in basil
and courgette“
P1410-RT

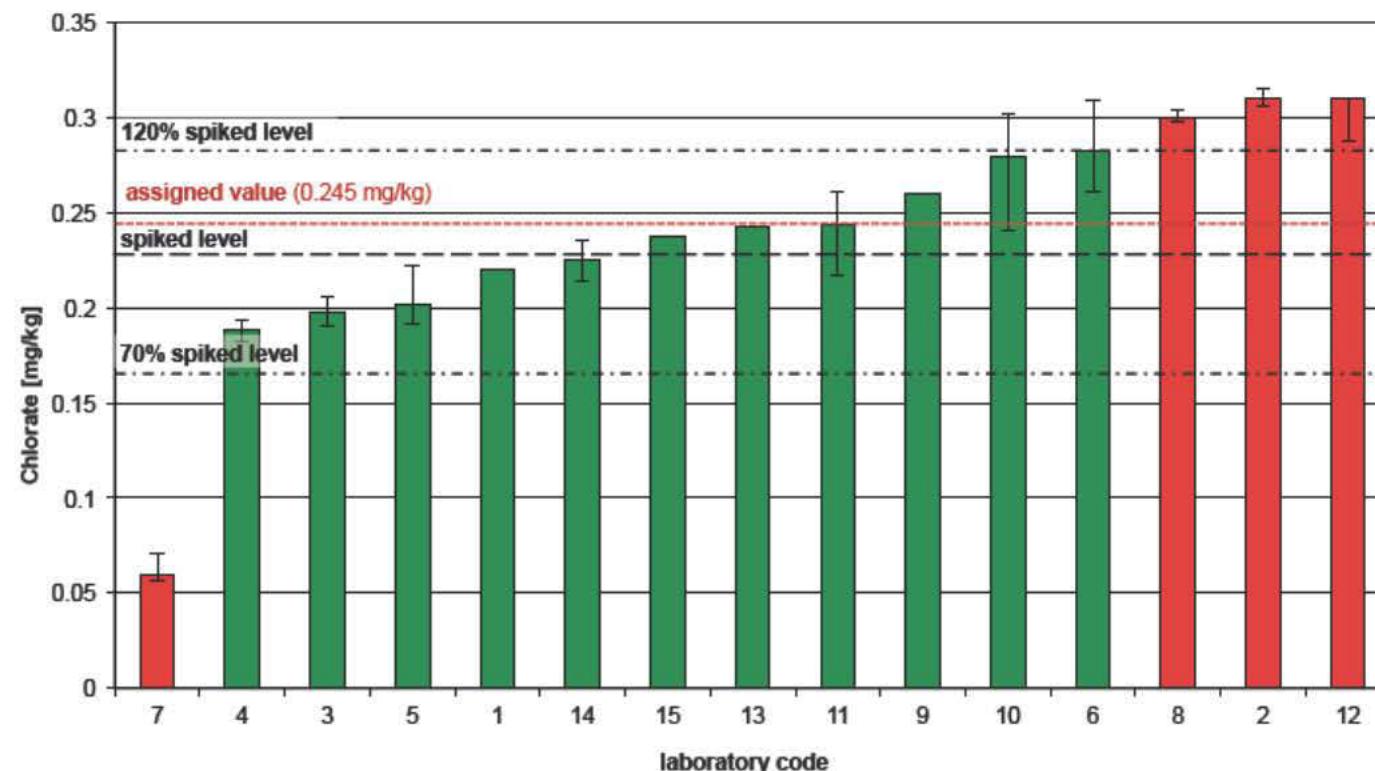
Report



CHLORAT (AND PERCHLORAT)

Method-Ringtest: Chlorat / basil

Figure 1. Chlorate in basil – assessment related to trueness

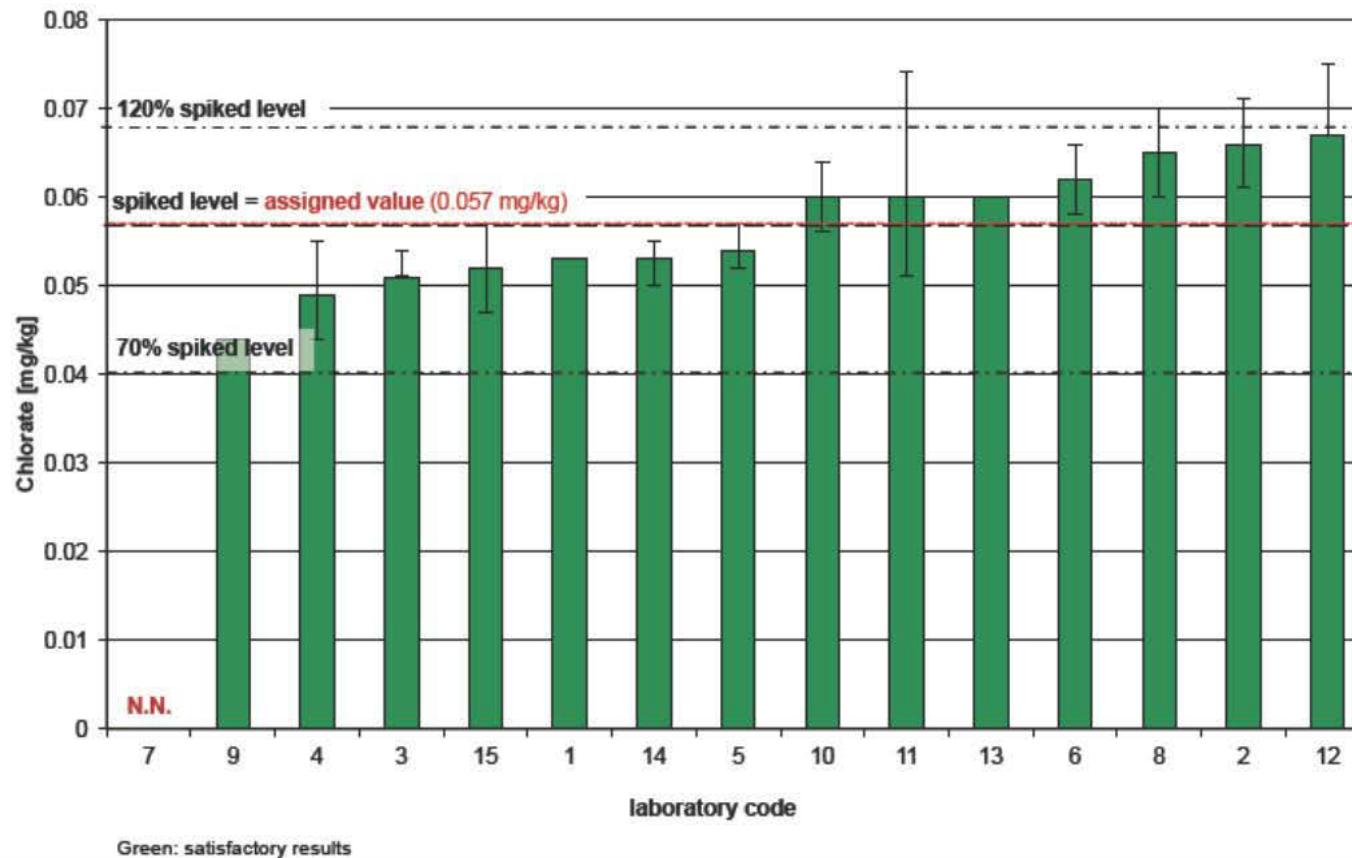


Green: satisfactory results, red: non-satisfactory results

CHLORAT (AND PERCHLORAT)

Method-Ringtest: Chlorat / courgette

Figure 2. Chlorate in courgette – assessment related to trueness



CHLORAT (AND PERCHLORAT)

Method-Ringtest „CHLORAT / PERCHLORAT“

Details:

[www.proof-acs.de/
competence_schemes0.html](http://www.proof-acs.de/competence_schemes0.html)

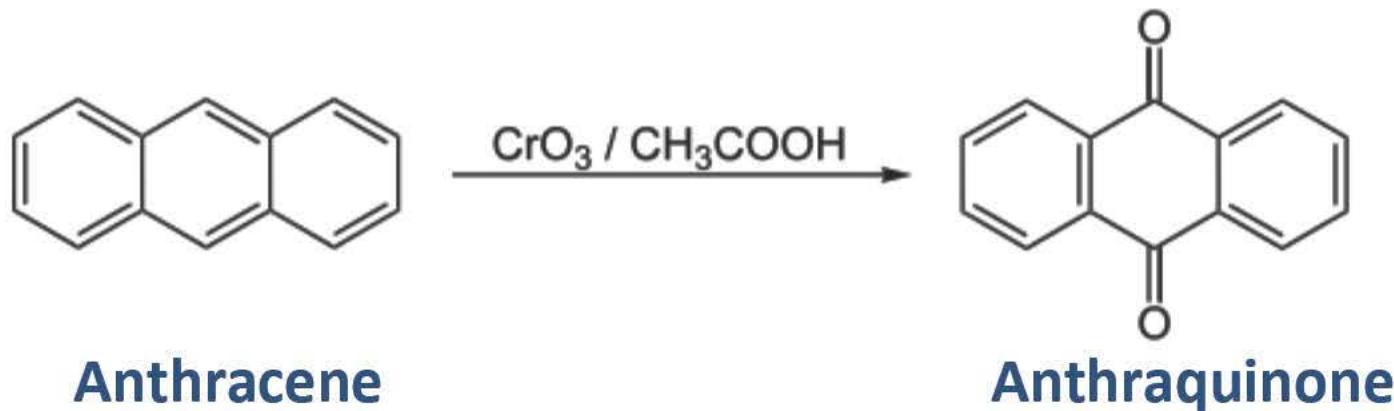
- Absatzzentrale Kempen GmbH, Kempen, Germany
- Analytica Alimentaria GmbH, Kleinmachnow, Germany
- Analytica Alimentaria GmbH, sucursal en Espana, Almeria, Spain
- Analytisches Institut Bostel GmbH & Co. KG, Stuttgart, Germany
- bilacon GmbH, Berlin, Germany
- Chemisches Institut Burkon, Nürnberg, Germany
- CLF Central Laboratories Friedrichsdorf GmbH, Friedrichsdorf, Germany
- Eurofins Institut Dr. Appelt Leipzig GmbH & Co.KG, Leipzig, Germany
- FYTOLAB cvba, Zwijnaarde, Belgium
- GREIT s.r.l., Bologna, Italy
- Institut Kirchhoff Berlin GmbH, Berlin, Germany
- Intertek Food Services GmbH, Bremen, Germany
- Labor Friedle GmbH, Tegernheim, Germany
- Laboratoire PHYTOCONTROL, Nimes, France
- Laboratorium Zeeuws-Vlaanderen B.V., Graauw, The Netherlands
- Landwirtschaftskammer Nordrhein-Westfalen LUFA NRW, Münster, Germany
- LUFA-ITL GmbH, Kiel, Germany
- LVA GmbH, Klosterneuburg, Austria

ANTHRAQUINONE / PAH



MOAH = mineral oil “aromatic” hydrocarbons

➤ „PolyAromatic Hydrocarbons“



ANTHRAQUINONE / PAH

TEA



Possible sources of contamination:

- ***Packaging*** (in the meantime less important)
- ***Environmental contamination*** (by poisoned air)
- ***Contamination during processing*** (drying, roasting)

ANTHRAQUINONE / PAH

TEA Contamination during processing (drying, roasting)



ANTHRAQUINONE / PAH

TEA

→ **New MRL for Anthraquinone:**
EU-regulation No. 1146/2014: 20 µg / kg

To be used from 18th May 2015 on.



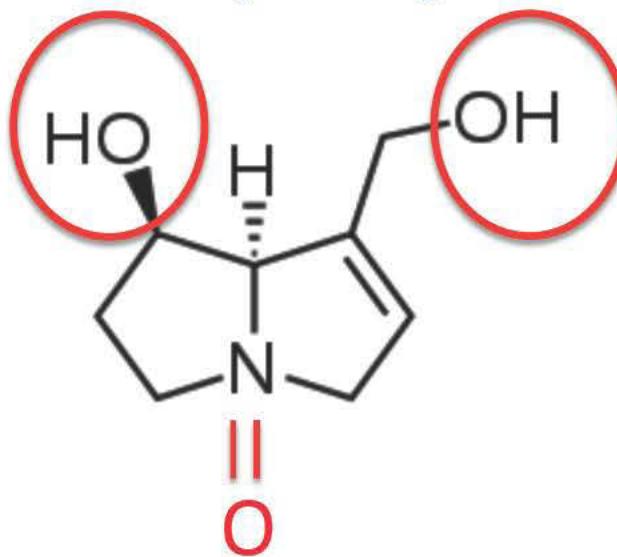
PYRROLIZIDINALKALOIDS (PA)

About 600 different PAs have been identified so far:

Basic structure: Retronecine

- Mono-Ester
- Di-Ester
- Cyclic Di-Ester

↓
*Increasing
Toxicity*



and additionally PA-nitrogen-oxides (PANO)

PYRROLIZIDINALKALOIDS (PA)

Occurance in about 6000 plant species (examples)

daisy family



orchidaceous



borage



*legumes (pulses)
family*



senecio

PYRROLIZIDINALKALOIDS (PA)

Analytics

Ring Test
 „Pyrrolizidine alkaloids in herbal teas“
 P1412-RT

Summary



Criterion	Short description of the criterion	Chamomile tea (5 spiked PA)	Mixed herbal tea (8 spiked PA)
<i>Identification</i>	All PA were <i>identified in the test material</i>	6 out of 7 laboratories (86 %)	6 out of 7 laboratories (86 %)
<i>Comparability</i>	The reported results of all PA are within a $z\text{-score} \leq 2 $	3 out of 7 laboratories (43 %)	4 out of 7 laboratories (57 %)
<i>Trueness</i>	The reported results of all PA are <i>within 70 to 120 % of the spiked level</i>	1 out of 7 laboratories (14 %)	1 out of 7 laboratories (14 %)
<i>False positive results</i>	The laboratory reported a false positive result of one or more PA	-	1 out of 7 laboratories (14 %)

The aim of this proficiency testing was the correct *identification* and *quantification* of a selection of the 17 "BfR-pyrrolizidine alkaloids":

Echimidine, Heliotrine, Heliotrine-N-oxide, Intermedine, Lasiocarpine, Lasiocarpine-N-oxide, Lycopsamine, Monocrotaline, Monocrotaline-N-oxide, Retrorsine, Retrorsine-N-oxide, Senecionine, Senecionine-N-oxide, Seneciphylline, Seneciphylline-N-oxide, Senkirkine, Trichodesmine.

PYRROLIZIDINALKALOIDS (PA)

ATTENTION:

Results are always related to the tested sample!

Analysing the next sample from the same (big) batch might show totally different results!

REASON:

The PA-containing plant species are not distributed equally - but randomly .

New contaminants

Pyrrolizidinalkaloids (PA)

Chlorat



Anthraquinone / PAH