Chlorate Residues in Plant-Based Food

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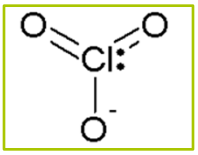
Introduction



Chlorates are effective as herbicides and disinfectants (biocides). Chlorate is also a by-product of using chlorine or chlorine dioxide for the disinfection of water.

Until 1992 several plant protection products containing sodium chlorate were authorized for use as herbicides in Germany, the most well-known of which was “Unkraut Ex”.

Since 2010, however, there has been an EU-wide ban on the application of plant protection products containing chlorate. In accordance with EU regulations, the standard maximum residue limit (MRL) of 0.01 mg/kg for unauthorized substances is valid for chlorate residues in food.

Following the inclusion of chlorate analyses in the QuPPe method as per the EURL-SRM, CVUA Stuttgart analyzed plant-based foods for chlorate residues in a special statewide monitoring program.

Parallel to the monitoring of chlorate, perchlorate is continuing to be analyzed as well, to investigate if there is any relationship between residues of chlorate and perchlorate.

Legal and toxicological aspects

No enforcement levels have been defined thus far; therefore, the standard MRL of 0.01 mg/kg is still valid. Samples whose chlorate content is verified as exceeding the MRL of 0.01 mg/kg may not be marketed. For the great majority of samples unwanted health problems (mainly negative effects on thyroid function and damage to the red blood cells) are not of concern, according to assessments made thus far. In a few samples (e.g. frozen broccoli and aubergines), however, acute health risks cannot be ruled out.

Analytical methods

Analyses were performed applying the QuPPe method and LC-MS/MS determination (ESI neg mode), using an $^{18}O_3$-Internal Standard (ILIS).

LC-Conditions:

Column:

• Hypercarb 2.1 x 100 mm; 5 µm

Mobile Phase:

• A: 1% acetic acid in water + 5% MeOH

• B: 1% acetic acid in MeOH

Gradient: 0 - 10 min 100% A - 70% A

Injection Volume: 5 µL; samples 5-fold diluted

Results

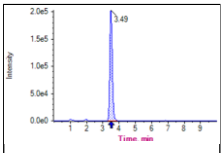
About 24% of more than 1,660 samples analyzed thus far have been found to contain chlorate residues in a range of 0.01 to 3.6 mg/kg.

The highest levels of chlorate measured were in aubergines from France (3.6 mg/kg) and two samples of deep-frozen broccoli (3.6 mg/kg and 2.5 mg/kg), their origin unknown. Interestingly, both of the broccoli samples had been labeled as organic. Among the samples from organic food production, about 12% contained chlorate residues exceeding the level of 0.02 mg/kg.

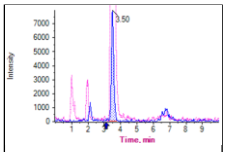
From April 2013 to May 2014:	No. of Samples	%
No. samples	1661	
No. chlorate findings > 0.02 mg/kg	199	12
No. chlorate findings > 0.1 mg/kg	51	3.1
No. chlorate findings > 0.25 mg/kg	26	1.6
No. chlorate findings > 0.50 mg/kg	16	1
No. chlorate and perchlorate findings (both ≥ 0.01 mg/kg)	143	8.6

In about 36% of the samples with chlorate residues (≥ 0.01 mg/kg) perchlorate residues (≥ 0.01 mg/kg) were also detected. High levels of chlorate did not necessarily correlate with high levels of perchlorate.

Chlorate in tomatoes at 0.005 mg/kg



ILIS Chlorate $^{18}O_3$ 89/71



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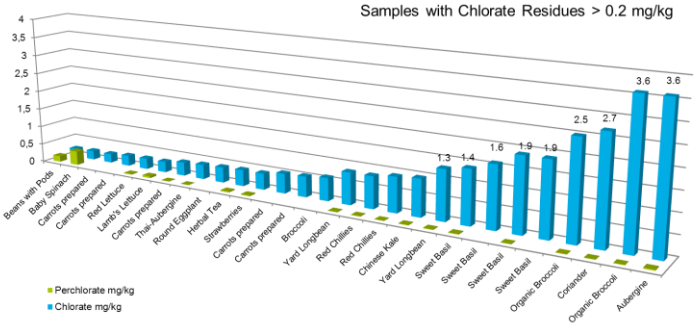

Summary

The cause of the residues has not yet been fully elucidated and investigations throughout the production chain are in process. Irrigation with chlorinated water may be one source of contamination, as well as post-harvest treatments using chlorinated water as a disinfectant during the Hydrocooling process. In the EU it cannot be precluded that unauthorized applications leading to the accumulation of chlorate residues are taking place. Monitoring will be continued.

Further information

Baden-Württemberg