Chlorate in Food

Occurrence, toxicity, maximum levels, analysis

A. What is Chlorate and what it is it used for?

Chlorates (ClO_3^{-}) are salts of chloric acid ($HClO_3$) and are strong oxidizing agents. They are used, for example, for bleaching paper or tanning leather. Chlorates also have herbicidal properties and were approved in Germany until 1992 in the form of sodium Chlorate as an active ingredient in plant protection products.



Structural formula of Chlorate

Since 2010, the use of plant protection products or biocidal products containing Chlorate as an active ingredient has been prohibited in all European Member States.

However, chlorate can be formed as a by-product when cleaning or disinfecting drinking water with chlorinecontaining solutions such as sodium hypochlorite.

B. Chlorate and perchlorate

Similar to Chlorate, Perchlorate (ClO_4) – salt of perchloric acid $(HClO_4)$ – also has oxidative capabilities. Perchlorate is used primarily in industrial chemicals, as a pharmaceutical and rocket fuel. Perchlorates are not approved as crop protection agents or as biocidal active ingredients, but they can be formed by disproportionation from the hypochlorites, chlorites and chlorates used for disinfection purposes and have been detected in numerous fruit and vegetable products.

C. Which foods contain Chlorate and why?

Chlorate was often found in frozen vegetables, fruit juices and salads/

herbs. The occurrence of Chlorate in these products can have processes reasons such as glazing of frozen foods, diluting juice concentrates or washing herbs and salads with water containing Chlorate.

Investigations were carried out at the Chemisches und Veterinäruntersuchungsamt Stuttgart, known as CVUA Stuttgart, which is the official surveillance laboratory of Baden-Wuerttemberg. They showed that plant-based foods (different types of fruit and vegetables) might contain Chlorate. Chlorate contents mainly resulted below 0.01 mg/kg (about 76% of the samples), but in some samples, also chlorate contents up to 2.7 mg/kg (e.g. coriander from Cambodia) were found. The causes or sources of the residues have not yet been finally clarified. The treatment of drinking water with chlorine-containing agents has been identified as one source of contamination. The CVUA Stuttgart also describes a possible further input path via chlorinated water, which was used for washing vegetables and fruit.

D. Is Chlorate harmful to health?

Depending on the dose, Chlorate can have a high acute toxicity to humans, especially on the oral pathway. This is primarily manifested by damage to the erythrocytes (red blood cells), resulting in methaemoglobin formation and haemolysis. In addition, the chronic intake of Chlorate can result in a reversible inhibition of iodide in the thyroid gland, which at higher doses can possibly lead to changes in thyroid hormone levels, especially in sensitive groups of people such as children, pregnant women or people with thyroid dysfunction. In a risk assessment from 2015, the EFSA (European Food Safety Authority) and the BfR (German Federal Insti-

tute for Risk Assessment) conclude that long-term exposure to Chlorate in food is potentially harmful to health, especially in children with mild to moderate iodine deficiency. However, it is unlikely that the total intake of a single day - even in the range of the highest estimated intake levels - will exceed the recommended safety level for consumers of all age groups. The new risk assessment for chlorate has therefore established a tolerable daily intake (TDI) of 3 µg/kg body weight per day for chronic exposure and an acute reference dose (ARfD) of 36 µg/kg body weight for acute exposure.

E. Are there maximum levels for Chlorate in food?

As an former active ingredient in plant protection products, chlorates are generally subject to the regulations of Regulation (EC) No. 396/2005 (Pesticide Regulation), which sets the maximum pesticide residues that may be present in animal and plant food and feed. These MRLs include specific MRLs for certain food and feed products and a general maximum residue level which applies where no specific MRL is set. As chlorates are no longer authorized as active substances since 2010 and no specific MRLs have been set, a maximum level of 0.01 mg/kg applies throughout the EU.

Since autumn 2018, discussions have been underway at EU level on setting specific maximum residue levels for Chlorate under Regulation (EC) No. 396/2005. Currently (as of February 2020) a draft regulation SANTE/10684/2015 in the version 8th revision is available. This draft regulation has been accepted by the Standing Committee (SC PAFF) on Plant Protection Residues at its last meeting on 17./18.02.2020.



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Specifically, the MRLs for fruit and vegetables, among other things, are to apply not only to fresh but also to frozen products (irrespective of whether there are new Chlorate entries between the fresh and frozen state). The MRLs for cocoa in the draft apply to cocoa beans (0.05 mg/kg).

The draft regulation in its 8th revision contains a so-called burden of proof for the legal assessment of processed foods; according to this, the burden of proof of additional Chlorate inputs in the context of food production or processing lies with the food manufacturer.

The regulation is expected to be published in the Official Journal of the European Union in autumn and will enter into force 20 days later without any transition periods (approx. September/October 2020).

F. How is chlorate analysed?

For the qualitative and quantitative determination of Chlorate in plantbased foods a single determination analysis method published by the European Reference Laboratories is available (EU Reference Laboratories for Residues of Pesticides – EURL-SRM, CVUA Stuttgart). In this method, the chlorates are extracted from the food sample with water and acidified methanol solution. The extract is then centrifuged, filtered and analysed by liquid chromatography coupled with mass spectrometry (LC-MS/MS).

G. Conclusion

Due to its high toxicity and the resulting negative effects on human health, Chlorate is undesirable in food. At the LCI, a method for the analysis of Chlorate and Perchlorate was recently developed and validated. This analysis can now be commissioned at our sister institute, the Institute for Quality Promotion in the Confectionery Industry in Cologne, IQ.Köln (contact: iq-koeln@iq-koeln.de).



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