Analysis of Cocoa Shell Today

Cocoa and chocolate products are very popular as a food and luxury food all over the world and the variety of chocolate products on the market is high. According to the BDSI (Federal Association of the German Confectionery Industry), 1,095,000 tons of high-quality chocolates and chocolate goods were produced in 2018.

Thus, the per capita consumption of chocolate goods lies above 9 kg per year, constant over many years, and chocolate goods represent the largest and most profitable market segment within the confectionery industry.

The cocoa shell content as a quality parameter

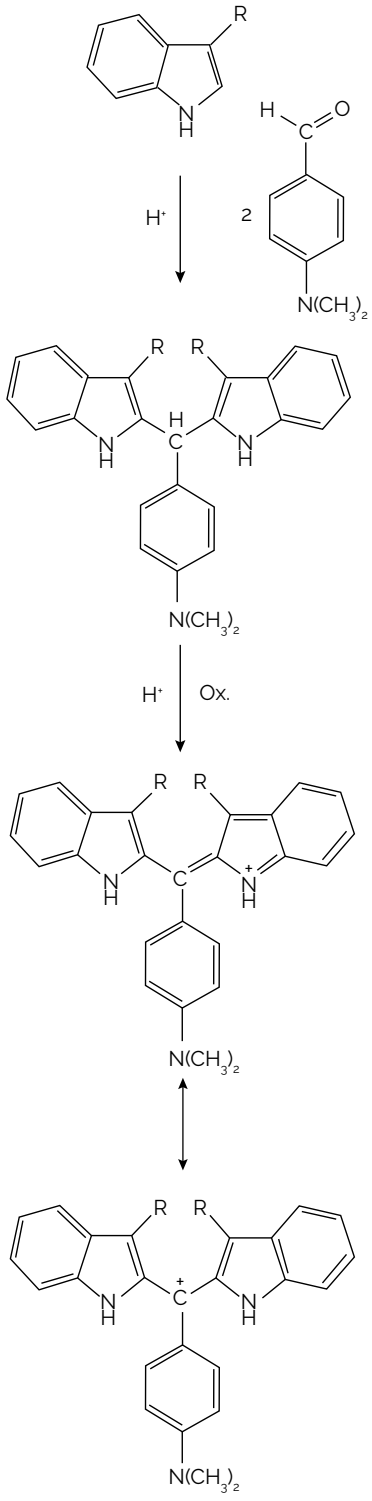
The proportion of shell has been considered an important quality parameter for products made from roasted cocoa beans for decades and more than ever today. In the quality assessment of cocoa products, the question arises to what extent shell-rich raw materials or overpressing are used during production. In the production process, undesirable substances can pass from the shell into the cocoa butter and adversely affect the aroma and crystallization properties of cocoa products. High levels of shells in the final product ultimately represent deterioration and are therefore unacceptable.

In this regard, the Codex Alimentarius Commission has established a benchmark level of 5 % cocoa shell, including the germs, calculated on the fat-free cocoa dry mass, which applies to both cocoa mass and cocoa presscake. If good manufacturing practice is followed, this value should not be exceeded in order to obtain a high quality and acceptable product. With its entry into force of the EU Cocoa Directive 2000/36/EC, the legal limit of the cocoa shell content in cocoa products in the EU has disappeared. Consequently, the 2003 German Cocoa Regulation does not contain a maximum quantity of cocoa shells in cocoa products.

Analysis of cocoa shell content

At the beginning of the 20th century, microscopic methods were used for the identification of characteristic cocoa mucus and stone cells in the analysis of cocoa shells. It is taken advantage of that stone cells occur in all cocoa varieties exclusively in the testa, the seed coat. As early as 1900, Fischer proposed a detection method in which it was possible to derive the shell content from the number of stone cells and their anatomy. However, these methods are today increasingly difficult to use because of the modern milling techniques, which make a large part of the characteristic stone cells invisible. In principle, all microscopic methods according to the current state-of-the-art analysis are considered extremely inaccurate, time-consuming and labor-intensive. However, the application of a matrix-based calibration curve and the use of a polarizing microscope have made the procedure considerably simpler, and the AOAC (Association of Official Agricultural Chemists) still considers the counting of stone cells (single or groups) to be the method of choice.

For purity testing of cocoa butter, the blue-value method developed by Fincke and Sacher in 1963 is widely used in industrial quality control (see figure 1). This method, also known as "B value", was published in the method collection of the IOCCC (International Office of Cocoa, Chocolate and Sugar Confectionery). In the blue-value method, fatty acid tryptamides and other substances with indole structure as indicator compounds for cocoa waste fats (fat from cocoa shell) react with p-Dimethylaminobenzaldehyde (p-DMAB) in an acidic medium to form a complex which is oxidized to a blue dye by hydrogen



Reaction scheme B value

peroxide. In particular, Behenic acid tryptamide (BAT) is found in high quantities in cocoa shells. By means of photometric measurement of the blue dye, a statement about the cocoa butter quality can be made. A blue value of <0.04 indicates a perfect cocoa butter.
Since the "B value" is a sum method whose specificity and selectivity no longer meets today's analytical standards, a new rapid method was developed at the Technical University of Munich in cooperation with the LCI in the years 1998–2000. The dominant fatty acid tryptamides BAT and LAT (Lignoceric acid tryptamide) are quantified as indicator substances using a powerful method based on high-performance liquid chromatography with fluorescence detection [HPLC-FLD].

Current developments in the field of cocoa shell analysis

The quantitative determination of the cocoa shell content is still one of the most important control investigations in cocoa products.
The LCI therefore carried out a scientific project in 2018 on the subject of "Cocoa Shell Analysis Today". The aim of this work was to fundamentally revise the "B-value" method, since Carbon tetrachloride (CCl_4) originally used as a solvent is highly undesirable for humans and the environment due to its harmful effects on human health and the environment. The possibility of using alternative solvents in exchange with CCl_4 was checked in a robustness determination. The comparison showed that hexane fulfills the criteria relevant for the determination of the "B value" and can therefore be exchanged for CCl_4. In addition, it was shown that the very time-consuming shaking by hand in routine analysis can be exchanged by extraction in an ultrasonic bath. This method, optimized for modern analysis, has been called the "Eco-B value" method. However, for the determination of the shell content in cocoa masses and cocoa powders, the determination of Fatty acid tryptamides (FAT) by means of HPLC-FLD is the state-of-the-art analytical method. Since FATs also occur in small quantities in cocoa kernels (cotyledons without seed coats), the shell content can still only be estimated. In addition, it is important to take into account analytical and biological variations, since the content of Tryptamide is influenced by various factors.
Between 2016 and the end of 2018, the FEI research project "Development of simple mass spectrometric methods for the quantitative detection of cocoa shells in cocoa products for routine analysis" searched for further indicator compounds in the cocoa shell under the direction of Markus Fischer at the University of Hamburg. High-resolution mass spectrometry was used to identify and characterize 18 key metabolites in cocoa shells that are suitable for determining the cocoa shell content in cocoa products using multivariate data analysis. To quantify these 18 metabolites from the classes Fatty acid tryptamides, 5-Hydroxy fatty acid tryptamides, -Tocopherol derivatives, Triacylglycerols and Ceramide derivatives, an LC-ESI triple quadrupole MS method was developed. However, none of the metabolites investigated meets the criterion of excludability for occurrence in the cocoa shell only, but is always also found in cocoa kernels in small amounts.
In summary, despite centuries of research into cocoa shell analysis, there is still no suitable analytical method for the exact quantification of the cocoa shell content in cocoa products. With the methods and innovations presented here, however, a satisfactory estimation of the cocoa shell content is achievable.

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