Detection of Titanium Dioxide in Food

Relevant for: Food Industry, Testing Laboratories, Regulatory Authorities

Raman spectroscopy is a rapid and easy method to identify titanium dioxide (E171), a white pigment widely used in the food and consumer goods industries.

1 Introduction

Titanium dioxide (TiO_2) is a white pigment which is used in paints, plastics, paper, pharmaceuticals, cosmetics, sunscreen, and toothpaste or as catalyst.[1, 2, 3]

In addition, it has been approved as a food additive (ingredient number E171) since 1969.[4] The main food categories containing titanium dioxide are candy, bakery wares (esp. icing and decorations), chewing gum, ice cream, and cheese.[2] Most food-grade titanium dioxide contains its anatase modification.[3] It is highly stable towards various conditions (e.g. heat, light, pH) and thus unaffected by almost every type of food processing.

The French Agency for Food, Environmental and Occupational Health & Safety found in 2019 that there was not enough evidence to prove titanium dioxide was safe for human consumption. In consequence, the French government bans titanium dioxide in food starting January 2020.[2, 6]

These concerns have arisen following recent studies which considered nanoparticles of TiO_2 to be harmful after oral intake.[3, 4] Experiments revealed that titanium dioxide is absorbed by the mammalian gastrointestinal tract.[4, 5] According to animal tests, it is a potential carcinogen.[1, 4, 5] As titanium dioxide is ubiquitous in foodstuff, a suitable and fast method to examine food products is needed. Since titanium dioxide is a very Raman-active material, Raman spectroscopy using the Cora 5001 is a suitable method for examining titanium dioxide in food products.

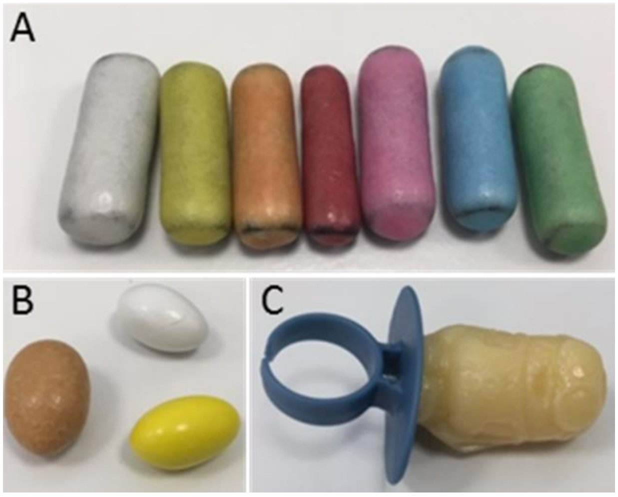

Figure 1: Measured food samples of sugar-coated licorice (A), sugar-coated peanuts (B), and a candy ring (C).

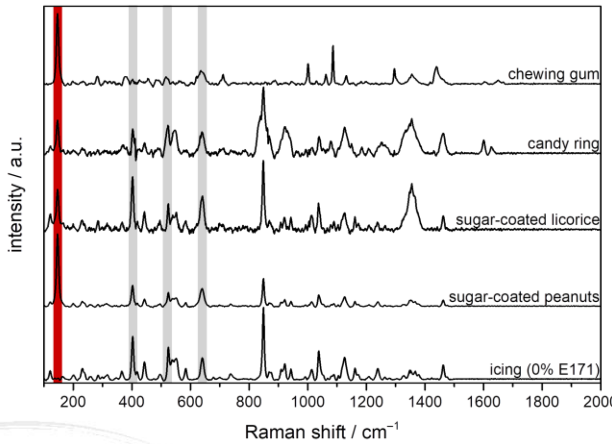

Figure 2: Raman spectra of different commercial food samples. The peak of interest to prove the presence of titanium dioxide is highlighted in red. Highlighted in grey are other peak positions of anatase which can also be present in products without TiO_2. As a reference icing without titanium dioxide (E171) was measured.

2 Experiment

2.1 Sample Preparation

Commercial samples of candy and sweets with the ingredient titanium dioxide (E171) were measured without further sample preparation. To determine the limit of detection and for quantification of titanium dioxide contents a calibration using icing was performed. Icing sugar and titanium dioxide in the anatase form were mixed with water. For lower titanium dioxide proportions icing with 0.5 % anatase or 1 % anatase and icing without titanium dioxide were mixed in different ratios. Samples were prepared in a range of 0 % to 1 % anatase. The icing samples were deposited on a microscopy slide and dried.

2.2 Instrumentation and Settings

Anton Paar's Cora 5001 Raman spectrometer with sample compartment was used to conduct the measurements. An excitation wavelength of 785 nm and a laser power of 450 mW were used. The acquisition time was determined by the software using the implemented auto exposure option. In addition, the subtract background option and baseline correction were activated. An excitation wavelength of 532 nm is also suited for titanium dioxide. However, sugar components may cause an increased fluorescent background with a laser source of higher photon energy.

With its spectral range for 785 nm of 100 cm^{-1} to 2300 cm^{-1} Cora 5001 is a versatile analytical tool for studying the presence and content of titanium dioxide in food matrices.

Samples were placed on the automated stage of the instrument and the focus rotor was placed in vertical orientation. Prior to measurements, a focus adjustment was performed using the implemented autofocus routine.

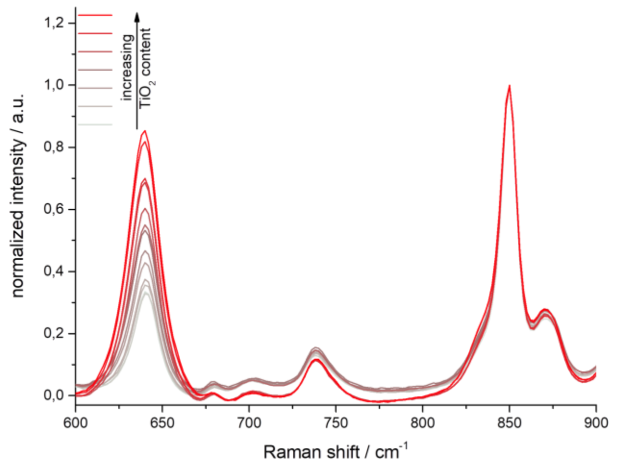

Figure 3: Rising peak due to increasing content of titanium dioxide for the tested icings (range 0% to1 % TiO_2) compared to a constant sugar signal.

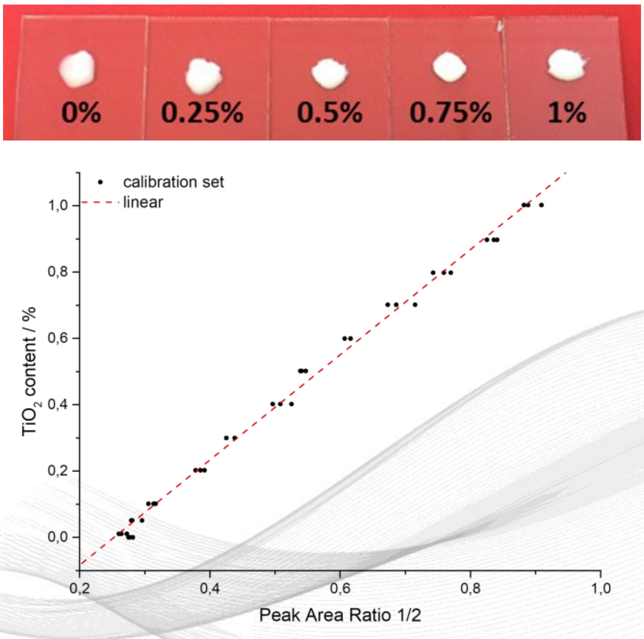

Figure 4: Examples of icing samples with different content of titanium dioxide (above) and related calibration curve (below). There is a linear correlation of the calculated peak area ratio and content of titanium dioxide.

3 Results

3.1 Identifying Titanium Dioxide in Food Products

As reported in another application report [7] anatase shows four main peaks at 143 cm^{-1}, 396 cm^{-1}, 514 cm^{-1} and 638 cm^{-1}. The peak at 143 cm^{-1} is the most pronounced and since most food-grade titanium dioxide contains anatase, it can be used to identify titanium dioxide in food products. Besides this, the rutile modification also shows a Raman peak at 143 cm^{-1}. However, it is less pronounced. The peak position at 143 cm^{-1} does not interfere with Raman signals of sugar which is the main component in most products with E171.

Different commercially available candy products (see Figure 1) which named titanium dioxide (E171) in the list of ingredients were measured using Raman spectroscopy. The resulting spectra are presented in Figure 2. Since most of the products' main component is sugar, an icing sample without titanium dioxide was measured as reference.

All samples except for the reference (w/o titanium dioxide) show a signal at 143 cm^{-1} (highlighted in red) originating from anatase which is a strong Raman scatterer. This causes a pronounced peak although its content is below 1 %. Therefore, the presence of this peak can be seen as evidence of the presence of titanium dioxide in the tested products.

3.2 Quantification of Titanium Dioxide Proportion and Limit of Detection

To test if a Raman band of titanium dioxide can not only be used to prove the presence of anatase in food products but also to quantify its content, experiments with icing containing different amounts of titanium dioxide were performed. Since titanium dioxide (E171) is mostly added to sugar-containing products, this type of sample is an easy approach to face the quantification as a binary system.

Samples in a range of 0 % to 1 % of anatase were measured which covers the usual amounts and limits of titanium dioxide in food. [8] For quantifications the custom model 'Simple Quantification Tool' can be used (for details see [9]). The settings used for this custom model to quantify the anatase content are listed in Table 1. As measurement parameters (e.g. focus, exposure time, etc.) can vary it is recommended to use relative quantification metrics (ratios).

Table 1: Settings for the 'Simple Quantification Tool' of Cora 5001 for quantification of anatase in icing.

Variable	Setting
Quantification metric	Peak Area Ratio 1/2
Peak 1	610-670 cm^{-1} (anatase)
Peak 2	800-900 cm^{-1} (sugar)

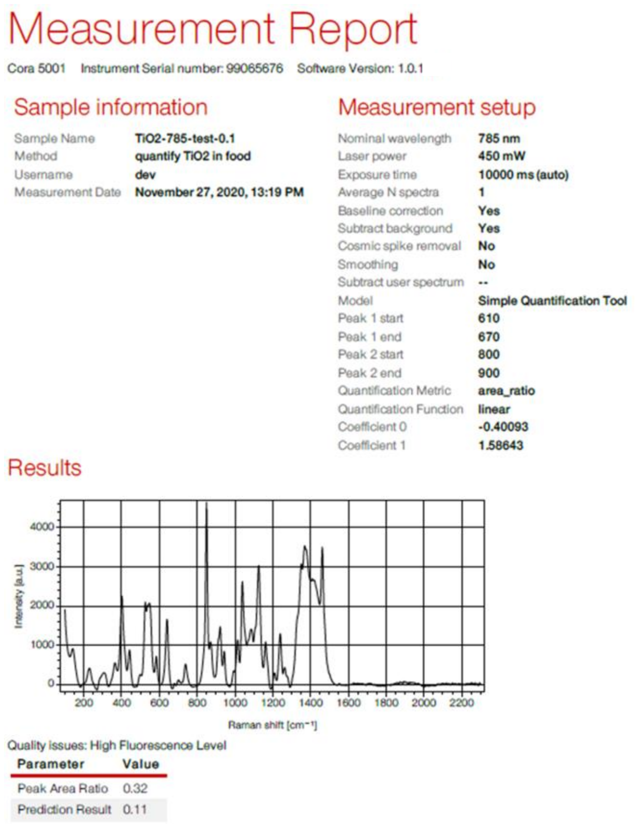

Figure 5: Report of a measurement with custom model showing all relevant data including the quantification result (see table below).

For quantification the second largest peak of anatase at 640 cm^{-1} was used and related to a pure sugar signal at 850 cm^{-1} (see Fig. 3) as the resulting limit of detection is lower for this peak. The content of titanium dioxide plotted against the corresponding peak area ratios gives a linear correlation (see Figure 4).

This offers the possibility to compare measured area ratios of unknown content of titanium dioxide to the calibration data to calculate the actual amount of anatase in the tested sample using the custom model. It directly shows the amount of titanium dioxide on the screen as well as in the result section of the measurement report (Fig. 5).

To calculate the limit of detection and quantification the reference sample of pure icing was measured ten times with the custom model. The limit of detection is 0.014 % anatase and the limit of quantification is 0.046 % anatase for the experiment of this report.

4 Summary

Raman spectroscopy performed with Cora 5001 is a simple method to prove the presence of titanium dioxide (here: anatase) in food products using one if its most pronounced Raman peak at 143 cm^{-1}. In addition, there is a linear correlation of the peak area ratio of anatase (640 cm^{-1}) and sugar peaks (850 cm^{-1}) to the titanium dioxide content that can be used for quantification. As limit of detection and quantification in sugar matrices 0.014 % and 0.046 % of titanium dioxide were calculated, respectively. The data needed for the calibration can easily be gathered using the Anton Paar custom model 'Simple Quantification Tool' on the instrument itself. Therefore, especially with regard to the ban of titanium dioxide as a food additive in France, Raman spectroscopy is a fast, easy, and non-destructive method for the quality control of food products.

5 References

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[6] https://www.tentamus.com/france-titanium-dioxide/?cn-reloaded=1; accessed 04.09.2019

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[8] M.-H. Ropers et al., IntechOpen, **2017**, DOI: 10.5772/intechopen.68883.

[9] Anton Paar Technical Note "Adding a Simple Quantification Model to Cora 5001", DocID E41IA028, **2020.**

Contact Anton Paar GmbH

Tel: +49 511 40095-0 | www.anton-paar.com

application-optotec@anton-paar.com