Gasochromic Detection of NO₂ on the Example of the Food Additive E141 (ii)[†]

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Abstract: We present our investigation on the gasochromic reaction of E141 (ii) towards the toxic gas nitrogen dioxide (NO₂). E141 (ii) is a chlorophyllin-based food additive, typically used as green coloring for nearly all kinds of sweets. In this presentation we show an alternative approach for using E141 (ii) as optical gas indicator. All solid samples are prepared by multi-layer screen printing on different substrates like paper and PE-foil. Gas measurements are performed using an UV/Vis spectrometer. The influence of the substrate and according layer thickness is shown.

Keywords: optical NO₂ detection; gasochromic color dye; copper chlorophyllin; screen printing

1. Introduction

The detection of the toxic gas nitrogen dioxide (NO₂) is of high relevance in varying fields like monitoring environmental pollution due to combustion or automotive emission, industrial safety or for early fire gas detection [1]. During the last few years, the approach of detecting gases by gasochromic dyes came to the fore. Several NO₂-sensitive color dyes are described in literature [2]; one of them is the characteristic green plant dye chlorophyll [3]. However, chlorophyll has the disadvantages of being very expensive and limited temperature stable. One promising alternative is the food additive Cu-chlorophyllin, also known as E141 (ii). According to the Commission Regulation (EU) No 231/2012 E141(ii): “The alkali salts of copper chlorophyllins are obtained by the addition of copper to the product obtained by the saponification of a solvent extraction of strains of edible plant material, grass, lucerne and nettle.”. E141 (ii) is of bright green color and used as coloring for confectionary, desserts, beverages, and ice cream etc.

The here presented approach shows the capability of E141 (ii) as color indicator for selective and reversible [2] NO₂ detection. The color change of E141 (ii) is recorded in solution and as screen printed test stripes on PE-foil and paper.

2. Experimental Part

For all experiments, E141 (ii) was used as color dye. It was provided by ExtraChem GmbH (Huchzermeierstr. 8a, 33611 Bielefeld, Germany), and consists of copper chlorophyllin (3.5–4.3%), maltodextrin, polysorbate 80 and potassium hydroxide. The sodium copper chlorophyllin is derived from a standardized and purified extract of grass or edible plant material. It is vegetarian, vegan, kosher and halal [4]. The chemical structure of sodium copper chlorophyllin is shown in Figure 1.

To demonstrate the color of E141 (ii) changes in the presence of NO_2 , 1 mg E141 (ii) were solved in 5 mL H_2O and exposed to 45 ppm NO_2 in dry nitrogen. For sample preparation, the color dye was transferred into a screen printing paste consisting of 15 g ethylcellulose, 15 mL tributylphosphate and 600 mL ethanol (99%). All educts are of pure grade and were provided by Sigma Aldrich (Darmstadt, Germany). The color dye concentration was set to 31 g/L. All samples were made by screen printing in order to get homogenous and thin layers, using a 180/27 screen in DIN A4. After printing, the samples were dried at room temperature for at least four hours. As substrates, paper (UPM Finesse Premium Silk, 150 g/m², UPM Communication Paper Augsburg, Germany) and PE-foil with ink adhesion primer (Autostat CT3, MacDermid, Wantage, UK) were used. To obtain different layer thicknesses, a multi-layer printing process was developed. It is divided into 1-layer (1nn: once printed wet-in-wet), 2-layer (2nn: twice printed wet-in-wet) and 3-layer (3nn: triple printed wet-in-wet). The resulting thicknesses were determined by 3D laser scanning microscopy (KEYENCE VK 9700 K, Keyence Deutschland GmbH, Germany) (for PE-foil): 2nn 0.9–1.1 μm and 3nn 1.5 μm .

Figure 1. Chemical structure of sodium copper chlorophyllin.

All measurements were performed at the gas measurement station of Fraunhofer IPM. The general description of the gas measurement station is given in [5]. The transmission spectra were recorded using a Perkin Elmer Lambda 900 UV/Vis-spectrometer (Perkin Elmer, Waltham, MA, USA).

3. Results and Discussion

To demonstrate the gas dependent color change of E141 (ii), 45 ppm NO_2 were passed through the solution. The reaction leads to a hypsochromic color change from bright green to pale yellow within 60 min as shown in Figure 2b. The related transmission spectra are given in Figure 2a. The reaction causes transmission changes in the violet ($\lambda = 410 \text{ nm}$) and orange ($\lambda = 630 \text{ nm}$) wavelength area.

The results of the PE-foil based samples to the reaction with NO_2 are shown in Figure 3. The samples were also exposed to 45 ppm NO_2 in dry N_2 . As in solution, the color changes induce signal changes within the violet and the orange wavelength area, comparing 2nn and 3nn layers. Compared to this, Figure 4 depicts the results of the reflection changes of the paper based samples, measured identically to Figure 3.

Table 1 summarizes the sensitivity to NO_2 (transmission change in %) of different samples depending on the layer thickness. It is obvious that the sample preparation, substrate and layer thickness have a remarkable influence to the sensitivity.

Figure 2. (a) Transmission spectra of dissolved E141 (ii) in H₂O before (green) and after (yellow) the reaction with 45 ppm NO₂ for 60 min. The color change increases the transmission within the violet (410 nm) and the orange (630 nm) wavelength area. (b) Photo of the E141 (ii) solution before (green) and after (yellow) treating with 45 ppm NO₂ for 60 min.

Figure 3. (a) Transmission spectra of screen printed E141 (ii) on PE-foil with different layer thicknesses (2nn and 3nn). The samples were exposed to 45 ppm NO₂ in N₂. (b) Picture of the test stripes on PE-foil before (up) and after (down) the exposure to 45 ppm NO₂.

Figure 4. Reflection spectra of screen printed E141 (ii) on paper with different layer thicknesses (1nn and 2nn). The samples were exposed to 45 ppm NO₂ in N₂.

Table 1. Overview of the sensitivity to 45 ppm NO₂ (given as the maximum transmission change in. %) of E141 (ii) in solution, screen-printed samples on paper as well as samples on PE-foil in dependency of the layer thickness.

	Layer	1 nn	2 nn	3 nn
solution	410 nm	9.2		
	630 nm	21.9		
paper	410 nm	3.9	5.1	
	630 nm	3.5	10.3	
PE-foil	410 nm		1.7	1.8
	630 nm		0.9	1.1

4. Conclusions

The capability of E141 (ii) as color dye for gasochromic NO₂ detection has been demonstrated. During NO₂ exposure, it changes its color from bright green to pale yellow. The intensity of this color change is significantly influenced by the sample preparation and layer thicknesses. As the pigment amount of copper chlorophyllin is limited to at least 4.3% of E141 (ii), this sensitivity is nevertheless remarkable. The use of pure copper chlorophyllin might further increase the sensitivity. Next steps are the integration of the color dye into a waveguide-based optical sensor set-up.

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