

## RED SYNTHETIC DYES IN TRADITIONAL SWEETS

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**Abstract:** The aim of this work was to determine red synthetic dyes in traditional sweets commercially sold at traditional open Easter market using high performance liquid chromatography. Four red synthetic dyes: azorubine (E122), amaranth (E123), cochineal red (E124), and Allura red (E129) were determined. On the basis of the results it was found that the most commonly used dye in traditional sweets was cochineal red – it occurred in 17 samples. Allura red was used only in one sample, whereas no sample contained azorubine. Six samples of sweets contained two kinds of red dyes. Amaranth and cochineal red contents ranged from 9.8 to 584.8 mg/kg and from 7.3 to 198.4 mg/kg, respectively. The maximum usage level of synthetic dye was exceeded only in one product, however most of the samples were incorrectly labelled, with lack of obligatory information about synthetic dyes used and that the synthetic dyes may have an adverse effect on activity and attention in children.

**Key words:** synthetic dyes, sweets, chromatography

### INTRODUCTION

Colour of food products is one of the basic quality factor concerned in the consumer food quality perception. Attractive colour encourages the purchase of food and affects perception of its tastiness. However, due to a possibility of degradation of the natural dyes during food processing and storage there is a need of use of dyes as food additives (**Pintea, 2008**). Use of organic synthetic dyes for dyeing of food should be monitored, therefore appropriate legal regulations and adequate analytical procedures should be used (**Socaciu, 2008; Kucharska, Grabka, 2010**). Synthetic dyes are commonly used in food technology in order to improve attractiveness of food products and to meet consumers' expectations. They are readily used by producers because they are characterised by greater resistance to environmental conditions, lower cost, higher productivity, standard strength of dyeing and more practical commercial form as compared to the natural dyes. Use of the synthetic dyes are relatively simple because they easily dissolve in water and have great colour variation (**Pintea, 2008**).

Among different adverse symptoms caused by synthetic dyes introduced to human body the neurobehavioural disorders, including attention deficit hyperactivity disorder (ADHD), are mentioned. According to the published reports, synthetic dyes including tartrazine, orange yellow, quinoline yellow, cochineal red, Allura red and azorubine can cause hyperactivity in children, especially when these dyes are present in products in which sodium benzoate is also present (**McCann et al., 2007**).

In the case of food products with food additives the labels must list these additives, give name or E number of each one, and also give information about basic technological function of the additives in food product. In response to study's results indicating adverse effect of synthetic dyes on child's body (**McCann et al., 2007**) the Regulation (EC) No 1333/2008 of the European Parliament and of the Council introduced a warrant that the labelling of food containing one or more of the above mentioned dyes shall include additional information, placed after name or E number of the dye, that it may have an adverse effect on activity and attention in children. In Poland, use of synthetic dyes in food processing are regulated by Regulation of the Minister of Health from 2010 that is consistent with EU legislation.

Determination and identification of synthetic dyes in food products are major challenges for analysts. Diversity of chemical structures, multitude of derivatives and presence of degradation products significantly impede qualitative and quantitative determination of synthetic dyes (**Kucharska, Grabka, 2010**). Another factor, that impedes analysis, especially extraction of dyes, is a possibility of interactions between dyes and native compounds of food product. To separate food dyes chromatographic methods are mainly used (**Kucharska, Grabka, 2010**).

The aim of this work was identification and quantitative analysis of red synthetic dyes present in traditional sweets using high performance liquid chromatography with detection in visible light.

## MATERIALS AND METHODS

Qualitative and quantitative determinations of synthetic dyes were done in nineteen red coloured sweets commercially sold at open Traditional Easters market. Four red dyes: azorubine (E122), amaranth (E123), cochineal red (E124) and Allura red (E129) (Hoffmann, Poland) were used as standard substances.

Calibration curves (Table 1) were performed with LaChrome high performance liquid chromatography system (Merck-Hitachi, Japan) equipped with UV-Vis detector. The solution concentration range was 1-50 mg/L. Mixture of methanol and 0.02 M ammonium acetate (at a ratio of 40:60) was used as an eluent in an isocratic elution at 1 cm<sup>3</sup>/min. The ODS Hypersil 250×4.6 mm, 5 μm (Thermo Scientific, USA) column was used and detection was performed at 512 nm. On the basis of calibration curves limit of detection (LOD) and limit of quantification (LOQ) were calculated (Table 1).

Weighted amount of sweet sample (5 – 20 g) was dissolved in deionized water at temperature of about 50 °C. The resulted solution was passed through the syringe filter (Millex LCR, PTFE, 0.45 μm) and then analysed in the chromatograph at the same conditions as used for the standard dye solutions. All measurements were done in three independent repetitions.

## RESULTS AND DISCUSSION

The dyes separated by chromatography were identified on the basis of the retention times of the chromatographic peaks. The retention times for amaranth and azorubine were 2.82±0.00 min and 17.89±0.73 min, respectively (Table 1). Values of limit of detection (LOD) and limit of quantification (LOQ) for the particular dyes ranged from 0.31 to 1.33 mg/L and from 0.93 to 3.99 mg/L, respectively (Table 1).

Table 1 Analytical parameters of the investigated synthetic dyes

Name of dye	Retention time (min)	Equation of the calibration curve	R <sup>2</sup>	LOD (mg/L)	LOQ (mg/L)
Azorubine (E122)	17.89±0.73	y = 60704 · x	0.9996	1.33	3.99
Amaranth (E123)	2.82±0.00	y = 52374 · x	1.0000	0.36	1.08
Cochineal red (E124)	3.37±0.01	y = 43853 · x	1.0000	0.45	1.35
Allura red (E129)	5.69±0.06	y = 70073 · x	1.0000	0.31	0.93

The amounts of dyes that exceeded LOQ were calculated on dye contents in mg/kg. On the basis of the results it was found that cochineal red was the most often present dye in the analysed samples (Table 2). This dye was found in 17 samples. Cochineal red contents in the samples were very diversified, with the lowest value (7.3 mg/kg) determined in sample 11, and the highest one (198.4 mg/kg) in sample 8. Amaranth was determined in 6 samples and its

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content ranged from 9.8 mg/kg in sample 2 to 584.8 mg/kg in sample 12. Next dye, Allura red, was detected and quantified only in product 18 (19.5 mg/kg). Azorubine was not present in any product. Only in product 16 no synthetic dye was present.

Table 2 Red synthetic dye contents in investigated traditional sweets

Sample number	Dye content (mg·kg <sup>-1</sup> )		
	Amaranth	Cochineal red	Allura red
1	-	194.2 ± 0.1	-
2	9.8 ± 0.7	23.5 ± 1.4	-
3	-	57.7 ± 0.4	-
4	-	181.5 ± 0.1	-
5	16.4 ± 0.1	32.7 ± 1.2	-
6	16.1 ± 0.0	32.3 ± 1.8	-
7	12.1 ± 0.2	10.8 ± 0.8	-
8	-	198.4 ± 1.9	-
9	-	23.7 ± 0.6	-
10	15.6 ± 0.2	12.2 ± 0.1	-
11	-	7.3 ± 0.1	-
12	584.8 ± 48.8	-	-
13	-	65.1 ± 2.2	-
14	-	193.8 ± 3.7	-
15	-	41.9 ± 1.5	-
16	-	-	-
17	-	47.1 ± 0.9	-
18	-	10.4 ± 0.2	19.51 ± 2.08
19	-	151.0 ± 10.8	-

Mean values from three determinations ± standard deviation

According to the existing legislation for confectionery (Legal act, 2010) synthetic dyes can be used individually or in combination in the amount not exceeding 300 mg/kg. With exception of one product (sample 12), all the other products met these requirements. Presence of amaranth that was found in the products 2, 5, 6, 7, 10 and 12 (Table 2) was not declared by the products' producers. In the case of sample 12 there was no list of components on the label. Moreover, in that product the amount of amaranth exceeded the permitted level. Cochineal red was determined in 17 products (Table 2), however its presence in a product was declared only in samples 8 and 17. In samples 9 and 11 presence of natural cochineal was declared, while the other samples did not have list of additives. Allura red was determined only in sample 18, however there was no information about its presence on the product label. Addition of azorubine and Allura red was declared for products 8 and 17, respectively, however our chromatographic analysis did not confirm presence of these dyes in the products.

In six analysed samples the presence of two dyes under study was found (Table 2). In product 2 amaranth and cochineal red were determined in the amount of 9.8±0.7 mg/kg and 23.5±1.4 mg/kg, respectively (Table 2). These two dyes were also present in samples 5, 6, 7 and 10. Sample 18 contained cochineal red and Allura red. Sum of the dyes contents did not exceed the allowed level in any product, however presence of these dyes was not declared on the products labels.

As a result of evaluation of the accordance of the label information with existing legislation for confectionery there were many incorrectness found, from which lack of basic information about product was the most frequent and stated for eleven products. Lack of

information about use of synthetic dye or incorrect information (inconsistency with the kind of dye) concerned seventeen products of nineteen ones analysed. Moreover, the product's labels did not contain obligatory statement that the synthetic dyes may have an adverse effect on activity and attention in children. This fault concerned all the products, with exception of product 16, in which presence of the analysed synthetic dye was not found. In several products the producers' declarations raised doubts. In the case of product 2, a presence of a natural cochineal, curcumin, which is characterized by yellow-orange colour, and chlorophyll complex were declared by the product's producer, while two synthetic dyes – amaranth and cochineal red – were determined. Addition of chlorophyll complex was also declared in the case of products 5, 6 and 7, while cochineal as a natural dye was declared for products 6, 7, 9 and 10, in which synthetic dyes were determined.

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