ELSEVIER

Journal of Food Composition and Analysis 18 (2005) 503–515

JOURNAL OF
FOOD COMPOSITION
AND ANALYSIS

www.elsevier.com/locate/jfca

Original Article

Determination of Carmoisine, Allura red and Ponceau 4R in sweets and soft drinks by Differential Pulse Polarography

S. Chanlon[a], L. Joly-Pottuz[a], M. Chatelut[a], O. Vittori[a,*], J.L. Cretier[b]

[a] *Laboratoire d'Electrochimie Analytique, Université Claude Bernard Lyon I, Bât. 308 - ESCPE, 43 Bd du 11 Novembre 1918, 69622 Villeurbanne Cedex, France*

[b] *Laboratoire des Sciences Analytiques UMR 5180, Université Claude Bernard Lyon I, Bât. 308 - ESCPE, 43 Bd du 11 Novembre 1918, 69622 Villeurbanne Cedex, France*

Received 3 September 2003; received in revised form 4 March 2004; accepted 19 May 2004

Abstract

Carmoisine (E 122), Ponceau 4R (E 124) and Allura red (E 129), are synthetic azo dyes 7generally used to give red colour to syrups, soda and sweets. They could be easily distinguished from the natural dyes, which are not electroactive, using differential pulse polarography. The influence of the pH on the intensities and the potentials of the peaks was studied between pH 3 and 11, and acidic or strongly basic media appeared not convenient. It was shown that in a pH = 9 phosphate buffer, the peaks of Carmoisine, Allura red and Ponceau 4R were well shaped and separated, allowing accurate identification and quantification, even if the three dyes were mixed. No significant changes of the peak potentials were noticed in the commercial samples, and consequently the dyes can be identified without ambiguity. A procedure using the standard addition technique was validated with test syrups. The recovery was in the 96–105% range and the relative standard deviation was close to 1% for the three dyes. The limits of quantification in the polarographic cell, estimated from the polarographic data, were 42, 43 and 34 $\mu g\,L^{-1}$ for Carmoisine, Allura red and Ponceau 4R, respectively. The method was applied to commercial soft drinks and sweets. The results were compared to those obtained using liquid chromatography, and they appeared to be in good agreement.

Keywords: Food dyes; Carmoisine; Ponceau 4R; Allura red; Differential pulse polarography; Liquid chromatography

*Corresponding author. Tel.: +33-4-72-43-14-13; fax: +33-4-72-44-84-79.
E-mail address: vittori@cpe.fr (O. Vittori).

0889-1575/$ - see front matter © 2004 Elsevier Inc. All rights reserved.
doi:10.1016/j.jfca.2004.05.005

1. Introduction

Synthetic dyes are commonly added to foods and beverages, and laws strictly control their uses and amounts. In France, the maximum amounts of the authorized synthetic dyes in syrups and sweets vary according to the nature of the dye. For syrups, they are usually ranging from 50 to 100 mg L^{-1}, but numerous commercial products are not in accordance, the dyes contents exceeding the allowed quantities. Thus, it appears necessary to identify and quantify with accuracy the dyes present in foods.

The numerous works published during the last years demonstrate the importance of this problem and the need for developing fast, accurate and selective techniques for synthetic dyes analysis. Chromatography, capillary electrophoresis, spectrometry and electrochemistry are usually used to perform dyes analysis, and each technique presents some advantages and inconveniences.

Chromatographic techniques have demonstrated their efficiency for many years (Hillman, 1975; Chudy et al., 1978; Berzas Nevado et al., 1997a, b; Gennaro et al., 1997; Chen et al., 1998), and they are still widely tested and improved (Vahey et al., 2000; Fuh and Chia, 2002; Capitan-Vallvey et al., 2002; Kirschbaum et al., 2003).

Capillary electrophoresis appeared more recently (Suzuki et al., 1994; Kuo et al., 1998; Berzas Nevado et al., 1999a, b; Frazier et al., 2000; Evans, 2003; Del Giovine and Piccioli Bocca, 2003) and Boyce (2001) has published a review about the determination of additives in food by capillary electrophoresis.

UV visible spectrometry is also a useful tool, but when two or more dyes are present, the overlapping of the peaks leads to difficult analysis. Moreover, it is impossible to distinguish easily between synthetic and natural dyes. In order to solve these difficulties, mathematical treatments of the spectra have been proposed (Saguy et al., 1978; Hofer and Jenewein, 1997; Capitan-Vallvey et al., 1998; Berzas Nevado et al., 1999a, b). Several recent papers demonstrate the interest of the UV–visible spectrometry (Kiroglu and Ozdemir, 2000; Capitan Vallvey, 2002; Altinoz and Toptan, 2003; Koyuncu et al., 2003).

Electrochemistry of azo compounds was studied many years ago (Florence, 1974; Thomas and Boto, 1975). Since 1979, Fogg et al., applied differential pulse polarography to azo dyes analysis (Fogg and Yoo, 1979) and their degradation (Fogg and Summan, 1983). The pH effect on the peaks potential was studied by Hart and Franklin Smyth (1980) and latter by Barros, which applied the technique to the dyes analysis in food, drugs and cosmetics (Barros Araujo et al., 1987, 1988). Becerro Dominguez et al. (1990) have demonstrated the sensitivity of DPP by determining 0.1–10 ppm of Sunset Yellow and Tartrazine in soft drinks. Azo dyes analysis was also successfully performed using stripping voltammetry at the mercury drop by Fogg et al. (1986), Castrillejo et al. (1990), Berzas Nevado et al., 1997a, b, Ni and Bai (1997), Barros et al. (1999), Zanoni et al. (1999), Zima et al. (2001), Guaratini et al. (2002) and Florian et al. (2002). Fogg and Bhanot (1981) applied voltammetric techniques using glassy carbon and carbon paste electrodes to the analysis of various dyes.

The purpose of this work was to find a suitable supporting electrolyte leading to a good separation of the DPP peaks of Carmoisine (E 122), Allura red (E 129) and Ponceau 4R (E 124), which are the most frequently synthetic red dyes added, alone or mixed, in soft drinks and sweets. The developed method based on standard addition procedure in a pH = 9 phosphate buffer supporting electrolyte, allows quick and accurate analysis of these dyes and appears specially well adapted for the control of excessive amounts.

Liquid chromatography, which is a well known and used technique for dyes determination, was used only as a complementary technique to validate the results.

2. Materials and methods

2.1. Reagents

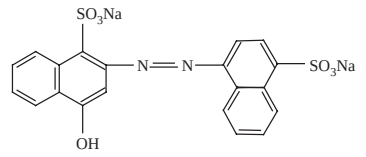
Mercury was hexadistilled by LAURYLAB. Potassium dihydrogen phosphate, orthophosphoric acid, triethylamine and methyl alcohol were of analytical grade and purchased from SIGMA-ALDRICH. The 0.2 M sodium hydroxide solution was prepared using an ampoule of sodium hydroxide. Solutions were prepared with distilled water. Buffers solutions were prepared by adding various volumes of 0.2 M NaOH to 100 mL of 0.1 M potassium dihydrogen phosphate and the pH was adjusted to the wanted value using a pH meter. The pH = 9 buffer solution was obtained by adding 50 mL of 0.2 M NaOH to 100 mL of 0.1 M dihydrogen phosphate.

Ponceau 4R (E 124, C.I. 16255, Food red 7) also named New Coccine or Cochineal red, was purchased from ACROS ORGANICS, Carmoisine (E 122, C.I. 14720, Food red 3) also named Azorubin or Chromotrope FB, was kindly offered by NEELIKON FOOD DYES, and Allura red (E 129, C.I. 16035, Food red 17) was purchased from ALDRICH (Fig. 1).

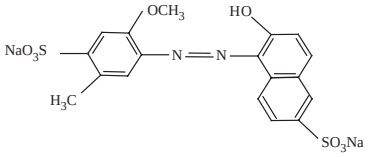
Standard stock solutions containing 100 mg L^{-1} of dye in distilled water were prepared.

2.2. Commercial samples

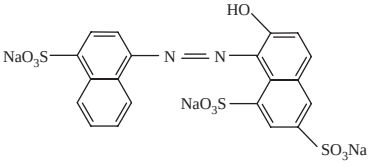
The method was applied to pomegranate syrups, non-alcoholic bitters, orange and grape fruit soda, and sweets. The major components of the syrups were sugar (about 800 g L^{-1}) and citric acid (about 8 g L^{-1}). They also contained glucose, fructose, fruits juices and sometimes flavours, and conservatives. The pH of the sodas and non-alcoholic bitters was found to be in the 2.5–2.9 range, and sometimes the fruits pulp made them turbid. The acid drops contained sugar, glucose,



Carmoisine E 122 M =502.44 g mol^{-1}



Allura red E 129 M = 496.3 g mol^{-1}



Ponceau 4R E124 M = 604.48 g mol^{-1}

Fig. 1.

hydrogenated vegetable fat, citric acid and aroma. In the case of gelled sweets, gelatine was added to the previous compounds.

Two low-priced pomegranate syrups were analysed. One was coloured with Ponceau 4R, the other with a mixture of Carmoisine and Ponceau 4R.

Two non-alcoholic bitters were tested, Ponceau 4R was present in the aromatic plants bitter and Carmoisine in the cherry bitter.

Two sodas, one blood orange and one pink grapefruit soda were coloured with Allura red.

The acid drops and the gelled sweets were coloured with Ponceau 4R.

2.3. Test syrups

Three commercial pomegranate syrups without synthetic dyes were tested, and it was verified that the natural fruits dyes were not electroactive. One of them was used to prepare two test syrups Ts1 and Ts2, by introducing known amounts of the three dyes.

2.4. Polarography

It is generally admitted (Kolthoff and Lingane, 1952) that azo molecules are reduced at the mercury drop in two steps. When the pH value is below 3, steps 1 and 2 occur simultaneously, while for media close to neutrality, the second step does not occur. Consequently, reduction potentials and intensities are strongly influenced by the media pH.

$$\text{R–N} = \text{N–R}' + 2e^- + 2H^+ \rightarrow \text{R–NH–NH–R}' \qquad \text{step 1,}$$

$$\text{R–NH–NH–R}' + 2e^- + 2H^+ \rightarrow \text{R–NH2} + \text{R}'\text{–NH2} \qquad \text{step 2.}$$

2.4.1. Apparatus

Measurements were performed using a computerized polarograph POL 150 + MDE 150 and the TraceMaster 5 software (RADIOMETER ANALYTICAL).

Differential pulse polarography (DPP) was performed with a falling mercury drop, a 2 s step duration and 2 mV amplitude step (equivalent to a 2 s drop time and a 1 mV s^{-1}scan rate). A 50 mV pulse was applied during 20 ms. The reference was an Ag/AgCl/3 M KCl/sat AgCl electrode and the auxiliary electrode was a Pt wire. The polarograms were recorded between −0.200 and −0.900 V (vs. Ag/AgCl).

The volume of supporting electrolyte in the cell was 10 mL, and oxygen was carefully removed by nitrogen bubbling during 300 s. All experiments were performed at room temperature (22°C). The peak intensities were determined using the TraceMaster 5 software after subtraction of the blank curve from the polarogram.

2.5. Chromatography

2.5.1. Apparatus

Experiments were performed by ion-pair liquid chromatography (HPLC) and photodiode array using a low-pressure chromatograph (Water), using a reverse-phase C_{18} column (Nova-Pak C18 from Waters) and gradient elution.

3. Results and discussion

3.1. DPP

The influence of pH on the polarograms was tested using various buffer solutions. For sake of simplicity an electrolyte made of dihydrogen sodium phosphate and sodium hydroxide was used here.

The influence of the phosphate buffers pH on the potentials and intensities of the peaks was tested with a solution containing 1 mg L^{-1} of each dye. The results are given in Table 1.

In buffers of pH < 7, the peaks of Allura red and Ponceau 4R were broad and small, and the peaks of the three dyes badly separated. When pH was higher than 10.5, the resolution between the peaks of Carmoisine and Allura was unsatisfactory. The best pH range in which reduction peaks of Carmoisine, Allura red and Ponceau 4R were well shaped and separated was 8–10. Except for Carmoisine, the sensitivity of measurements was maximum in pH = 9 buffer, so this value was selected for this study. Moreover in pH = 9 electrolyte, small amounts of commercial samples do not significantly change the pH, allowing the constancy of the peaks potentials. Higher value was not chosen in order to insure the safety of the glass capillary that is very sensitive to basic media.

A typical polarogram of a three dyes mixture is given in Fig. 2.

The calibration curves were established in pH = 9 phosphate buffer by increasing progressively the dye concentration in the cell with the standard stock solution. They were done essentially in order to define the concentration linearity range and the slope of the current/concentration straight line. The limits of quantification (LOQ) were estimated, although the major purpose of this work was to detect excessive amounts of dyes. The obtained data are reported in Table 2.

3.2. Samples preparation for DPP analysis

All dilutions were made with the buffer solution. The syrups were twice diluted, using a glass-gauged pipette, to reduce the high viscosity caused by the large amount of sugar. After dilution, they could be introduced in the polarographic cell using automatic micropipettes with satisfying

Table 1
Influence of the phosphate buffer pH on the peaks potentials and intensities of the azo dyes at 1 mg L^{-1} level

pH	Potential (V vs. Ag/AgCl)			Intensity (nA)		
	Carmoisine E 122	Allura red E 129	Ponceau 4R E 124	Carmoisine E 122	Allura red E 129	Ponceau 4R E 124
6.0	−0.300	−0.412[a]	−0.614[a]	231	77	99
7.0	−0.367	−0.498[a]	−0.688	225	101	143
8.0	−0.421	−0.560	−0.708	231	158	217
9.0	−0.472	−0.596	−0.732	236	231	291
10.0	−0.530	−0.625	−0.750	268	173	279
11.0	−0.584	−0.658	−0.770	237	125	206

[a] Bad-shaped peaks.

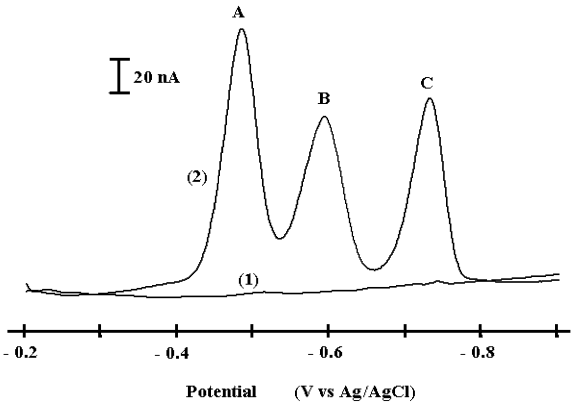


Fig. 2. Typical polarogram of a three dyes mixture in pH = 9 phosphate buffer. (1) : blank polarogram; (2) : polarogram of the dyes mixture: A : Carmoisine (0.6 mg L^{-1}); B : Allura Red (0.4 mg L^{-1}); C : Ponceau 4R (0.4 mg L^{-1}).

Table 2
Polarographic data of the red dyes in the pH = 9 phosphate buffer

Dye	Linearity range (mg L^{-1})	Slope (nA/mg L^{-1})	Intercept (nA)	R	LOQ (μg L^{-1})
Carmoisine E 122	0.02–4.0	236.1	0	0.999	42
Allura red E 129	0.02–4.5	230.9	0	1.000	43
Ponceau 4R E 124	0.02–4.0	291.2	0	0.998	34

R: correlation coefficient.
LOQ: Limit of quantification in the cell estimated for $S/N = 5$.

accuracy. The sodas and bitters were analysed without previous dilution or filtration. Acid drops were ground and 10 g of the powder were dissolved in 100 mL of the buffer. Two gelled sweets were accurately weighed (usually about 15 g), and dissolved in 50 mL of the buffer by moderate heating; after cooling the volume was adjusted to 100 mL with the buffer.

3.3. Analysis procedure

The complex composition of the samples may cause changes in the calibration slopes and, for this reason, the dyes concentrations were determined using the standard addition technique with two additions of the standard stock solution.

The blank polarogram of the supporting electrolyte was first recorded. Next, according to the sample concentration, 50–500 μL of the unknown solution were added in the polarographic cell and the polarogram done. A known amount of the standard stock solution was then added in the cell and the polarogram was recorded. This operation was done once more. To obtain accurate results, the final dye concentration in the cell was always in the linearity range determined previously.

As noticed all the commercial beverages were acidic, and to avoid any important changes in the pH, the amounts introduced in the polarographic cell must be lower than 1 mL. If the dye

concentration was too low for sensitive measurements, the introduced volume could be more important but in this case, previous neutralization of the sample was needed.

The dyes concentrations were obtained using the regression curves calculated with the Excel software (Microsoft). Five determinations were done for each sample, and the standard deviations were calculated.

3.4. Test syrups analysis procedure

Two ways of determination were investigated using the standard addition procedure described above.

First, the amount of each dye was determined one after the other, one sampling was used for each dye determination (called: separate measurements). Four polarograms are required for the quantification of each dye, which means twelve polarograms for the three dyes.

The amounts of the three dyes were also determined using only one sampling of the test syrup (called simultaneous measurements). In this case, the stock solution contained the three dyes, and only 4 polarograms were necessary to determine the concentrations of the three dyes.

3.5. Experimental results

When the test syrups Ts1 and Ts2, containing a mixture of the three azo dyes and natural substances, were introduced in the pH 9 electrolyte, it was noticed that the potential and the intensity of the Carmoisine peak were unchanged. For Allura red, a small potential shift was observed and, in the case of Ponceau 4R a larger potential shift and a large intensity decrease were noticed. Despite these observations, the separation of the three peaks remained very satisfying, and the accuracy of the determination was not lowered since the standard addition technique was used here.

The results obtained are given in Table 3a for separate measurements and b for simultaneous measurements.

It appeared that the good separation of the peaks due to the pH constancy allowed in all cases accurate measurements. The agreement between the values obtained by independent and simultaneous measurements demonstrate the interest of the second procedure.

The commercial samples were analysed following the same procedure. The obtained results are listed in Table 4a and b.

4. HPLC

4.1. Sample preparation for HPLC measurements

All dilutions were made using distillate water. The syrups were diluted ten times and the bitters five times. The sodas were analysed without previous dilution but the pulp had been removed by filtration. Acid drops were ground and 10 g were dissolved in 50 mL of water. Gelled sweet were cut in small pieces and 10 g were dissolved, without heating, in 50 mL of a pH = 2.5 orthophosphoric acid solution.

Table 3
Concentrations of the dyes in the test syrups determined by (a) separate and (b) simultaneous measurements using DPP and standard addition

(a) Separate measurements Dye	Peak potential (V vs. Ag/AgCl)	Provided ($mg\,L^{-1}$)	Found ($mg\,L^{-1}$)	Recovery (%)	s.d. ($mg\,L^{-1}$)	R.S.D. (%)
Ts1						
Carmoisine	−0.470	12.5	13.0	104.0	0.2	1.54
Allura red	−0.570	12.5	13.1	104.8	0.2	1.37
Ponceau 4R	−0.692	12.5	12.5	100.0	0.2	1.60
Ts2						
Carmoisine	−0.470	40.0	38.9	97.2	0.4	0.98
Allura red	−0.570	40.0	38.2	95.5	0.4	1.04
Ponceau 4R	−0.692	40.0	39.9	99.7	0.5	1.25

(b) Simultaneous measurements Dye	Provided ($mg\,L^{-1}$)	Found ($mg\,L^{-1}$)	Recovery (%)	s.d. ($mg\,L^{-1}$)	R.S.D. (%)
Ts1					
Carmoisine	12.5	12.5	100.0	0.2	1.6
Allura red	12.5	12.3	98.4	0.2	1.5
Ponceau 4R	12.5	12.6	100.8	0.2	1.7
Ts2					
Carmoisine	40.0	39.5	98.7	0.4	1.0
Allura red	40.0	40.2	100.1	0.4	1.0
Ponceau 4R	40.0	39.5	98.7	0.5	1.4

s.d.: Standard deviation calculated from five intra-day independent measurements.
R.S.D.: Relative standard deviation calculated from five intra-day independent measurements.

4.2. Analysis procedure

According to Fuh and Chia (2002), the mobile phase was composed of a 3×10^{-3} M solution of triethylamine adjusted to pH 6.5 by orthophosphoric acid addition (A) and methyl alcohol (B). The initial proportion was 90% A and 10% B and the applied gradient was 3% up to 30% A and 70% B. The column temperature was 22°C, the flow rate $1\,mL\,min^{-1}$. 20 μL of the sample solution were injected for each measurement. Spectrophotometric detection was performed at the maximum absorbance wavelength of the dye.

Analyses were made using calibration curves, established from the peak area as a function of dye concentration.

The retention times, wavelength and calibrations data are reported in Table 5.

The dyes concentrations in the commercial samples were determined by five intra-day measurements and the mean value calculated. The results are listed in Table 6a and b.

Table 4
Concentrations of the dyes in the (a) soft beverages and (b) red sweets determined by independent and simultaneous measurements using DPP and standard addition

Sample	Dye	Found (mg L^{-1})	s.d. (mg L^{-1})	R.S.D. (%)
(a) Soft beverages				
Pomegranate syrup 1	Ponceau 4R	223.1	4.1	1.8
		34.2 (separate)		1.2
	Carmoisine		0.4	
		30.8 (simultaneous)		1.3
Pomegranate syrup 2				
		72.5 (separate)		2.7
	Ponceau 4R		2.0	
		71.0 (simultaneous)		2.7
Aromatic plants bitter	Ponceau 4R	78.0	1.9	2.4
Cherry bitter	Carmoisine	3.7	0.1	2.7
Blood orange soda	Allura red	7.8	0.2	2.6
Pink grapefruit soda	Allura red	1.80	0.06	3.3
(b) Red sweets				
Acid drop	Ponceau 4R	19.6	0.2	1.0
Gelled sweet	Ponceau 4R	35.2	0.4	1.1

s.d.: Standard deviation calculated from five intra-day independent measurements.
R.S.D.: Relative standard deviation calculated from five intra-day independent measurements.

Table 5
HPLC data of the red dyes

Dye	Retention time (min)	Wavelength (nm)	Slope[a] (a.u./mg L^{-1})	Intercept (a.u.)	R
Ponceau 4R (E 124)	6	508	43781	0	0.9999
Allura red (E 129)	8	510	64106	0	0.9999
Carmoisine (E 122)	11	519	44506	0	0.9998

R: correlation coefficient.
[a] In the linear range (up to 25 mg L^{-1}).

5. Discussion

The results obtained by DPP and by HPLC, were compared in Table 7a and b.

A satisfying agreement of the found dyes amounts was observed, even in pomegranate syrups and gelled sweets despite the large amount of sugar in the first case, and gelatine in the second one. The necessary dilution of these samples to be in the linearity range strongly diminishes the influence of these compounds. So HPLC and DPP were equally useful analytical tools. For HPLC, which proceeds usually with calibration curves, the matrix effects may be an error source. The standard addition technique used in DPP seems a better way for determination of dyes in

Table 6
Concentrations of the dyes in the (a) soft beverages and (b) sweets determined by HPLC measurements

Sample	Dye	Found ($mg\,L^{-1}$)	s.d. ($mg\,L^{-1}$)	R.S.D. (%)
(a) Soft beverages				
Pomegranate syrup 1	Ponceau 4R E 124	209.8	1.7	0.08
	Carmoisine E122	39.1	1.6	4.1
Pomegranate syrup 2				
	Ponceau 4R E 124	68.5	2.2	2.9
Aromatic plants bitter	Ponceau 4R E 124	75.9	1.2	1.6
Cherry bitter	Carmoisine E 122	4.3	0.1	2.3
Blood orange soda	Allura red E 129	8.5	0.2	2.3
Pink grapefruit soda	Allura red E 129	1.57	0.01	0.06
(b) Sweets				
Acid drop	Ponceau 4R E 124	21.1	1.0	5.7
Gelled sweet 1	Ponceau 4R E 124	33.1	1.2	3.6

s.d. standard deviation calculated from five intra-day measurements.
R.S.D.: Relative standard deviation calculated from five intra-day independent measurements.

Table 7
Concentrations of the dyes in the (a) soft beverages and (b) sweets determined by DPP and HPLC

Sample	Dye	Found ($mg\,L^{-1}$)		E (%)
		DPP (separate)	HPLC	
(a) Soft beverages				
Pomegranate syrup 1	Ponceau 4R E 124	223.1	209.8	+6.0
	Carmoisine E122	34.2	39.1	−14.3
Pomegranate syrup 2				
	Ponceau 4R E 124	72.5	68.5	+5.5
Aromatic plants bitter	Ponceau 4R E 124	78.0	75.9	+2.7
Cherry bitter	Carmoisine E 122	3.7	4.3	−16.2
Blood orange soda	Allura red E 129	7.8	8.5	−9.0
Pink grapefruit soda	Allura red E 129	1.8	1.6	+11.0
(b) Sweets				
Acid drop	Ponceau 4R E 124	19.6	21.0	7.1
Gelled sweet 1	Ponceau 4R E 124	35.2	33.1	6.0

E = relative difference between DPP and HPLC measurements.

complex media, because it takes in accounts the matrix effects. Another advantage of DPP was observed with soda containing fruit pulp, since the curves may be recorded without filtration. Inversely, for HPLC, filtration was absolutely necessary, with the risk of a preadsorption of the dye on the filter, lowering the measured content.

6. Conclusions

This work demonstrates that differential pulse polarography, performed in an appropriated electrolyte such as the pH = 9 phosphate buffer, allows to distinguish synthetic Carmoisine, Ponceau 4R and Allura red from the natural red dyes, and separates them from one another.

The procedure using only one sample for all dyes determination represents a new and interesting way for minimizing the measurements duration without loss of accuracy.

As it eliminates the need for time-consuming sample preparation, it appears to be a rapid and accurate technique for dyes control in industrial beverages and sweets, and it can be a suitable alternative to HPLC technique.

References

Altinoz, S., Toptan, S., 2003. Simultaneous determination of Indigotin and Ponceau-4R in food samples by using Vierordt's method, ratio spectra first-order derivative and derivative UV spectrophotometry. Journal of Food Composition Analysis 16 (4), 517–530.

Barros Araujo, A., Cabral, J.O., Fogg, A.G., 1988. Use of gelatin in the differential-pulse polarographic determination and identification of synthetic coloring matters in drugs and cosmetics. Analyst 113 (6), 853–858.

Barros, A.A., Rodrigues, J.A., Almeida, P.J., Rodrigues, P.G., Fogg, A.G., 1999. Voltammetry of compounds confined at the hanging mercury drop electrode surface. Analytica Chimica Acta 385 (1–3), 315–323.

Becerro Dominguez, F., Gonzalez Diego, F., Hernandez Mendez, J., 1990. Determination of sunset yellow and tartrazine by differential pulse polarography. Talanta 37 (6), 655–658.

Berzas-Nevado, J.J., Guiberteau-Cabanillas, C., Contento-Salcedo, A.M., 1997a. Separation and determination of dyes by ion-pair chromatography. Journal of Liquid Chromatography and Related Technology 20 (18), 3073–3088.

Berzas Nevado, J.J., Rodriguez Flores, J., Villasenor Llerena, M.J., 1997b. Adsorptive stripping voltammetry (ASV) of tartrazine at the hanging mercury drop electrode in soft drinks. Fresenius' Journal of Analytical Chemistry 357 (7), 989–994.

Berzas Nevado, J.J., Guiberteau-Cabanillas, C., Contento-Salcedo, A.M., Martin-Villamuelas, R., 1999a. Spectrophotometric simultaneous determination of amaranth, ponceau 4R, allura red and red 2G by partial least squares and principal component regression multivariate calibration. Analytical Letters 32 (9), 1879–1898.

Berzas Nevado, J.J., Guiberteau Cabanillas, C., Contento Salcedo, A.M., 1999b. Method development and validation for the simultaneous determination of dyes in foodstuffs by capillary zone electrophoresis. Analytical Chimica Acta 378 (1–3), 63–71.

Boyce, M.C., 2001. Determination of additives in food by capillary electrophoresis. Electrophoresis 22 (8), 1447–1459.

Capitan-Vallvey, L.F., Fernandez, M.D., De Orbe, I., Avidad, R., 1998. Simultaneous determination of the colorants tartrazine, ponceau 4R and sunset yellow FCF in foodstuffs by solid phase spectrophotometry using partial least squares multivariate calibration. Talanta 47 (4), 861–868.

Capitan-Vallvey, L.F., Valencia, M.C., Nicolas, E., Arana, 2002. Flow injection analysis with on-line solid phase extraction for spectrophotometric determination of Ponceau 4R and its subsidiary unsulfonated dye in sweets and cosmetic products. Mikrochimica Acta 138 (1–2), 69–76.

Castrillejo, Y., Pardo, R., Barrado, E., Sanchez Batanero, P., 1990. Determination of food additive azo dyes at an HMDE with adsorptive stripping voltammetry. Electroanalysis (NY) 2 (7), 553–558.

Chudy, J., Crosby, N.T., Patel, I., 1978. Separation of synthetic food dyes using high-performance liquid chromatography. Journal of Chromatography 154 (2), 306–312.

Chen, Q.-C., Mou, Shi-Fen, Hou, Xiao-Ping, Riviello, J.M., Ni, Zhe-Ming., 1998. Determination of eight synthetic food colorants in drinks by high-performance ion chromatography. Journal of Chromatography A 827 (1), 73–81.

Del Giovine, L., Piccioli Bocca, A., 2003. Determination of synthetic dyes in ice-cream by capillary electrophoresis. Food Control 14 (3), 131–135.

Evans, L., 2003. Separation and quantitation of components in FD&C Red No. 3 using capillary electrophoresis. Journal of Chromatography A 991 (2), 275–280.

Florence, T.M., 1974. Polarography of azo compounds and their metal complexes. Electroanalytical Chemistry and Interfacial Electrochemistry 52, 115.

Florian, M., Yamanaka, H., Carneiro, P.A., Zanoni, Boldrin, M.V., 2002. Determination of brilliant blue FCF in the presence and absence of erythrosine and quinoline yellow food colours by cathodic stripping voltammetry. Food Additives & Contaminants 19 (9), 803–809.

Fogg, A.G., Yoo, K.S., 1979. Direct differential-pulse polarographic determination of mixtures of the food coloring matters tartrazine-Sunset Yellow FCF, tartrazine-Green S and Amaranth-Green S in soft drinks. Analyst 104 (1241), 723–729.

Fogg, A.G., Bhanot, D., 1981. Further voltammetric studies of synthetic food coloring matters at glassy carbon and carbon paste electrodes using static and flowing systems. Analyst 106 (1265), 883–889.

Fogg, A.G., Summan, A.M., 1983. Further differential-pulse polarographic and visible spectrophotometric studies of the degradation of permitted synthetic food colouring matters with and without the addition of ascorbic acid: degradation in the dark and in the light without the stabilising action of EDTA. Analyst 108 (1292), 1339–1344.

Fogg, A.G., Barros, A.A., Cabral, J.O., 1986. Differential-pulse adsorptive stripping voltammetry of food and cosmetic synthetic colouring matters and their determination and partial identification in tablet coatings and cosmetics. Analyst 111 (7), 831–835.

Frazier, R.A., Inns, E.L., Dossi, N., Ames, J.M., Nursten, H.E., 2000. Development of a capillary electrophoresis method for the simultaneous analysis of artificial sweeteners, preservatives and colors in soft drinks. Journal of Chromatography A 876 (1 + 2), 213–220.

Fuh, M.-R., Chia, K.-J., 2002. Determination of sulphonated azo dyes in food by ion-pair liquid chromatography with photodiode array and electrospray mass spectrometry detection. Talanta 56 (4), 663–671.

Gennaro, M.C., Gioannini, E., Angelino, S., Aigotti, R., Giacosa, D., 1997. Identification and determination of red dyes in confectionery by ion-interaction high-performance liquid chromatography. Journal of Chromatography A 767 (1 + 2), 87–92.

Guaratini, C.C.I., Zanoni, M.V.B., Fogg, A.G., 2002. Cathodic stripping voltammetric detection and determination at a hanging mercury-drop electrode of dye contaminants in purified biomaterials: study of the human serum albumin and reactive dye 120 system. Microchemical Journal 71 (1), 65–72.

Hart, J.P., Franklin Smyth, W., 1980. Polarographic behaviour and analysis of some azo dyes of biological significance. Analyst 105 (1255), 929–938.

Hillman, Robin A.H., 1975. Chromatographic investigation of food colorings in Smarties. School Science Review 56 (197), 763–765.

Hofer, K., Jenewein, D., 1997. Quick spectrophotometric identification of synthetic food colorants by linear regression analysis. Food Research and Technology 204 (1), 32–38.

Kirschbaum, J., Krause, C., Pfalzgraf, S., Bruckner, H., 2003. Development and evaluation of an HPLC-DAD method for determination of synthetic food colorants. Chromatographia 57 (Suppl.), S/115–S/119.

Kiroglu, F., Ozdemir, Y., 2000. Derivative spectrophotometric determination of carmoisine and ponceau 4R or Sunset Yellow in binary mixtures. Advances in Food Sciences 22 (3/4), 86–91.

Kolthoff, I.M., Lingane, J.J., 1952. In Polarography, Vol. 2. Interscience Publishers, New York, p. 768.

Koyuncu, I., Uzgur, M.U., Bozdogan, A., 2003. Comparison of partial least-squares multivariate spectrophotometric and derivative spectrophotometric method for the determination of food dyes sunset yellow (E-110) and tartrazine (E-102) in powder drinks. International Journal of Chemistry 13 (1), 19–23.

Kuo, K.L., Huang, H.Y., Hsieh, Y.Z., 1998. High-performance capillary electrophoretic analysis of synthetic food colorants. Chromatographia 47 (5/6), 249.

Ni, Y., Bai, J., 1997. Simultaneous determination of Amaranth and sunset yellow by ratio derivative voltammetry. Talanta 44 (1), 105–109.

Saguy, I., Mizrahi, S., Kopelman, I.J., 1978. Mathematical approach for the determination of dyes concentration in mixtures. Journal of Food Science 43 (1), 121–123, 134.

Suzuki, S., Shirao, M., Aizawa, M., Nakazawa, H., Sasa, K., Sasagawa, H., 1994. Determination of synthetic food dyes by capillary electrophoresis. Journal of Chromatography A 680 (2), 541–547.

Thomas, F.G., Boto, K.G., 1975. In: Saul Patai, (Ed.), The electrochemistry of azoxy, azo and hydrazo compounds. Wiley, New York, p. 443 (Chapter 12).

Vahey, P.G., Park, S.H., Marquardt, B.J., Xia, Y., Burgess, L.W., Synovec, R.E., 2000. Development of a positive pressure driven micro-fabricated liquid chromatographic analyzer through rapid-prototyping with poly(dimethylsiloxane). Optimizing chromatographic efficiency with sub-nanoliter injections. Talanta 51 (6), 1205–1212.

Zanoni, M.V.B., Carneiro, P.A., Furlan, M., Duarte, E.S., Guaratini, C.C.I., Fogg, A.G., 1999. Determination of the vinylsulfone azo dye, remazol brilliant orange 3R, by cathodic stripping voltammetry. Analaytica Chimica Acta 385 (1–3), 385–392.

Zima, J., Barek, J., Moreira, J.C., Mejstrik, V., Fogg, A.G., 2001. Electrochemical determination of trace amounts of environmentally important dyes. Fresenius' Journal of Analytical Chemistry 369, 567–570.