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Photoacoustic spectroscopy as a tool for determination of food dyes: Comparison with first derivative spectrophotometry

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ABSTRACT

Photoacoustic spectroscopy (PAS) was applied as a method to quantify dyed food samples, and was compared with First Derivative Spectrophotometry (FDS). The dyes Brilliant Blue (B), Sunset Yellow (S) and Tartrazine (T), which are common food additives, were employed for the comparisons. Polyester-type Polyurethane (PU) foam was used for extraction of the dyes from a solution containing the food matrix. For the spectrophotometric determinations, the adsorbed dyes were recovered by using dimethylformamide. The PAS measurements were carried out directly on the PU foam. The PAS method showed greater sensitivity, with detection limits of 0.028 mg L^{-1} and 0.086 mg L^{-1} for S and T, respectively, in the S+T mixture, and of 0.012 mg L^{-1} and 0.068 mg L^{-1} for B and T, respectively, in the B+T mixture. The values of relative error obtained for all the dyes were small: ~0.3–3.6% for the spectrophotometer, and ~0.1–2.9% for the PAS method. The PAS technique can be applied to the determination of the selected dyes in commercial food products, with some advantages: it reduces the number of analysis steps, it is a "green" method with less chemical waste, a minimal sample amount is needed, and it is non-destructive.

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1. Introduction

Bright, colorful and stable synthetic dyes are widely added to food to replace the natural colorants that can be lost in processing, and to reduce batch-to-batch variations in manufactured products. However, some synthetic colorants may be toxic, especially if consumed in large amounts. Therefore, the presence of many dyes in foods must be controlled, and in order to prevent their indiscriminate use, regulations have been developed by many countries limiting types and amounts of dyes, which may be expressed as the Acceptable Daily Intake (ADI) [1–3].

Several analytical procedures have been used in the determination of food dyes, especially chromatography, spectrophotometry and voltammetry [4–8]. Spectrophotometry is frequently used for dye determination, but intense overlapping is quite common in analyzing a mixture of dyes. Therefore, the direct absorption measurement is not suitable for resolving dye mixtures without a preliminary separation step. Derivative spectrophotometry is an analytical technique of great utility for obtaining information from spectra that show unresolved bands. However, because the differentiation degrades the signal-to-noise ratio, some form of smoothing is required [9]. Derivative techniques have proved to be very useful in the resolution of binary and ternary mixtures [10,11], and, recently, quaternary mixtures of dyes [12]. Even though these methods are capable of resolving multi-component color in foods, some of them show limitation over a wide range of pH values. For example, the chromatographic method is only suitable for pH over 4.8 [13], and a spectrophotometer is not able to resolve a mixture of two or more components. On the other hand, the First Derivative Spectroscopy (FDS) method is claimed to be able to resolve food colorants prepared in buffer solution with pH lower than 4.8 [14]. Capillary Zone Electrophoresis (CZE) can determine food colorants at very high pH ~ 11.0 for the buffering solution. In CZE, the most important factor is the choice of buffer pH and the buffering capacity at that pH [15].

Photoacoustic spectroscopy (PAS) is a non-destructive technique based on photothermal phenomena, which allows spectroscopic studies, thermophysical parameter assessment, and depth profile analysis of materials. PAS has been used for diverse applications in different areas, including studies in the material, environmental, and life sciences [16–21]. Since PAS is a sort of absorption spectroscopy, it is useful for dyed samples; for example,

Abbreviations: ADI, acceptable daily intake; FDS, first derivative spectroscopy; CZE, capillary zone electrophoresis; PAS, photoacoustic spectroscopy; PU, polyurethane; LOD, limit of detection.

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photoacoustic spectroscopy has been applied in the analysis of a single-component food dye. Recently, Dóka et al. [22] successfully applied the PAS method in the study of multi-vitamin tablets containing powdered food-colorant Sunset Yellow. Their report suggested the PAS as a suitable candidate for quality testing of synthetic dyes, but did not test foodstuffs with more than one component.

In the present study, photoacoustic spectroscopy is compared to the derivative spectrophotometry, aiming to resolve binary mixtures of food colorants; the techniques were applied to determinations of the Brilliant Blue, Sunset Yellow, and Tartrazine dyes.

1.1. Photoacoustic spectroscopy

The general heading of photoacoustic or photothermal phenomena implies the generation of acoustic waves or other thermoelastic effects by an incident modulated radiation beam. Nowadays, photoacoustics encompasses acoustic and thermal detection techniques, and has been successfully applied to many problems in physics, chemistry, biology, medicine and engineering [21]. The main advantages are the versatility in the detection systems that use either microphone (up to a few kHz) or piezoelectric sensors (up to MHz). Another factor is the sensitivity to very small temperature variations between 10^{-6} °C and 10^{-5} °C when power excitation is at least 10 μW/cm^2, which is typical power for some specific visible wavelengths selected from a white lamp. The capability for depth profile inspection allowing studies of layered material, in addition to the non-destructive analysis, is a great advantage. Moreover, more than one component of absorbing species in foodstuffs containing mixed food dyes can be detected, since any absorption band can be tracked in the material at different absorbing wavelengths.

Almost all conventional optical spectroscopies are based on one of the two main approaches [16]: (i) study of optical photons that are transmitted trough the sample, without any interaction with the constituents of the sample; (ii) study of scattered or reflected photons that have had some interaction with the constituents of the sample. The conventional transmission or reflection types of optical spectroscopy are inadequate when very weak absorption is involved in spectroscopic measurements, once one works with very strong transmitted, reflected or scattered signals. Although developments have been done on these techniques, such as derivative spectroscopy, this inadequacy is still remained. On the other hand, PAS deals with direct measurements of the energy absorbed by the constituents of the sample as a result of its interaction with the photon beam.

Several theoretical models for the photoacoustic effect in solids have been developed [16–21], of which the Rosencwaig–Gersho theory is the most commonly used [23]. This model is a one-dimensional analysis of the photoacoustic signal in a cylindrical geometry consisting of a solid sample in a small, gas-filled cell, at a fixed distance from a transparent window through which a modulated radiation beam is incident. The principle of PAS is the heating produced in a sample due to the absorption of a modulated incident radiation beam. The absorption of this incident beam and the subsequent non-irradiative de-excitation processes give rise to a heat source in the sample. The periodic heat flow from the sample to the surrounding gas causes periodic heating of the boundary layer of gas, which acts like a piston, and generates acoustic waves in the cell.

A typical PAS assembly is represented in Fig. 1. It consists of a light source, a monochromator, a light modulator (chopper), a photoacoustic cell with a condenser microphone, a lock-in amplifier and a data acquisition system. Efficient light sources provide strong photoacoustic signals; in the visible spectral range, high-output xenon or xenon–mercury lamps are usually used. In PAS, the signal is produced by pressure variation in the photoacoustic cell, and it is detected by a microphone mounted on the cell wall. As mentioned above, this pressure variation occurs because the incident radiation beam is modulated. The most common method for modulation uses a mechanical chopper. Since pulses are generated and absorption is occurring at the same frequency, it turns out that the heat transfer process will result in a photoacoustic signal at the same chopping frequency, which usually ranges between 10 Hz and 3000 Hz. The lock-in amplifier is used to amplify the PAS signal at the chopping frequency, raising the signal-to-noise ratio. Diaphragm condenser microphones with flat frequency response are most commonly used for detecting the acoustic signals produced in the gas-filled cell. For details and complementary reading, the reader may refer to literature [16–24].

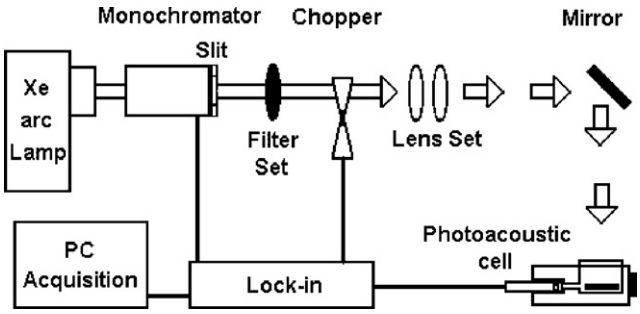

Fig. 1. Experimental configuration for PAS measurements.

The periodic heat flow from the sample to the surrounding gas, in the photoacoustic cell, depends on: the amount of the incident radiation absorbed by the sample; the light-to-heat conversion efficiency; and the heat diffusion through the sample. Therefore, PAS can be used as a thermal and optical characterization technique, because the detected photoacoustic (PA) signal is a result of optical absorption, and will be dependent on the optical absorption coefficient. On the other hand, it is also dependent on heat transfer, and as a consequence it varies with thermal properties including the thermal diffusivity and thermal conductivity of the material.

In this study, the possibility of applying PAS as a quantitative method for food-colorant determination was evaluated. The optical properties were examined in accordance with the Rosencwaig–Gersho theory [23]. Photoacoustic spectra of individual food colorants and of binary mixtures were obtained in the spectral range of 300–750 nm and then compared with the absorption spectra of the same colorant species in solution.

2. Experimental

2.1. Reagents

Brilliant Blue (CI 42090), Sunset Yellow (CI 15985) and Tartrazine (CI 19140) commercial dyes (Duas Rodas Industry, Santa Catarina, Brazil) were purified to over 85% purity (89% for CI-15985 and 91% for CI-19140) by means of successive extractions with different high-grade organic solvents; the final products were dried at 60 °C for 12 h. The purity was determined by comparison with tabulated data from the literature [25]. The dye working solutions were freshly prepared from the stock solutions (1000 mg L^{-1}) by diluting an appropriate weight of each colorant with deionized distilled water. The buffer solution (pH 3.0) was prepared from 1.0 mol L^{-1} acetic acid to adjust the conditions for fixing the colorant onto polyester-type polyurethane (PU) foam. All solvents and reagents were of analytical grade. The PU foam (d = 60 kg m^{-3}) was washed with water and acetone, and dried before use. The foam pieces were ground in a stainless-steel container with a blender, to pass a 150 μm sieve.

2.2. Procedure for dye determination in foods

A volume of 10.0 mL of the sample solution was transferred to a 25.0 mL volume balloon diluted, and then 10.0 mL of CH_3COOH (at 2.0 mol L^{-1}) was added. The pH of this mixture was adjusted to 3.0 with NaOH (at 1.0 mol L^{-1}). Then, 150 mg PU was added to 10.0 mL of the buffered sample solution, and the mixture was stirred (with a magnetic stirrer) for 20 min and then centrifuged. Next, the mixture was filtered and the PU foam dried for 30 min at 60 °C. For the spectrophotometric measurements, the dyes were recovered with N,N-dimethylformamide, and the colorants in these sample solutions were then determined as described below. For the photoacoustic determination, PU foam samples with adsorbed dyes were used. Blanks and standard solutions were prepared and treated in the same way as described for the samples.

2.3. Food sample treatment

Derivative spectrophotometry and photoacoustic spectroscopy were applied to determine Brilliant Blue (B), Sunset Yellow (S) and Tartrazine (T) dyes in commercial products. The solutions of gelatine powder (peach and lemon flavors, dissolved in hot water at 60 °C) and juice powder (citrus fruit flavor, dissolved in water, at room temperature) were constituted according to their label recommendations, and were filtered in a 0.45 μm mesh filter.

2.4. Method based on first derivative technique

The absorption spectra of the samples and binary standard mixtures (containing up to 10 mg L^{-1} of each dye) were recorded between 400 nm and 700 nm with a scan rate of 350 nm min^{-1} (Hitachi U-2000 Spectrophotometer). First derivative spectra were obtained with a $\Delta\lambda = 3$ nm and smoothing over 11 experimental points, using Savitzky-Golay simplified method [9]. The signal at the zero-crossing points for the binary mixtures was measured, and, using appropriate working curves, the concentration of each dye in the different mixtures was determined.

2.5. Method based on photoacoustic spectroscopy

For the photoacoustic measurements, we used a white light beam (Xe arc lamp, 800 W) passed throughout a monochromator (200–800 nm) and modulated (mechanical chopper, 20 Hz) before it reached the photoacoustic cell (shown in Fig. 1). The strategy of analysis was to apply the spectral de-convolution from Gaussian peaks for the individual substances first, by fixing the wide absorption band centers and the areas of each Gaussian peak. Therefore, in the binary mixtures, the pair of overlapping bands is given by a balanced summing over the Gaussian peaks

$$S(\lambda) = a\sum_{m} G_{m,x}(\lambda) + (1-a)\sum_{n} G_{n,y}(\lambda),$$

where a is the balance parameter, and m (n) is the number of Gaussian peaks used to fit the PAS absorption band of the pure substance x (y). Each Gaussian peak is modeled as

$$G(\lambda) = I_0 + \left[\frac{A}{w\sqrt{\pi/2}}\right] \cdot \exp\left[-\frac{\sqrt{2}(\lambda-\lambda_c)}{W}\right]^2,$$

where I_0 is the absorption value of the base line, A is the area of the Gaussian peak, λ_c is the wavelength value corresponding to the Gaussian curve maximum, and w is the Gaussian curve half-width.

This methodology allowed us to select the best conditions for analysis of the binary mixtures, and the photoacoustic signals were determined at the maximum of the peak with the least contribution from the other peaks [26].

3. Results and discussion

Prior to applying PAS to the study of multi-component commercial foodstuffs containing dyes, we recently developed a methodology using polyurethane foam as a dummy sample doped with colorants. That study indicated the capability of PAS to discriminate individual dye components based on their absorption spectra in binary-doped foam [27]. Therefore, these results led us to apply this methodology in the study of multi-colorant content in commercial foods such as gelatin and juice powders, in which the flavors and colors are based on added colorants. Foodstuffs based on food colorants are complex materials, and from the point of view of spectroscopy they can be viewed as a simple binary system, with part of them being a matrix (backbone) and the other being a complement such as doping, colorant, or modifiers. For spectrophotometric studies, a contribution from the background of this "matrix" is always present, which interferes with the analysis of the other components [14].

It is suggested that the adsorption of dyes in PU foam occurs when the species (colorant) is predominant in the neuter form, and the adsorption of each species is a combination of steric effects and the inductive and hydrophobic nature of the species [14]. The use of PU foam has attracted attention because of the good results obtained with procedures of separation/preconcentration of organic and inorganic species [27].

In this study, PUF was used in order to adsorb the colorants from the solution with the food matrix for further analysis. Next, these PU pieces containing the food colorants were also used as a backbone material for spectroscopic analysis through their optical absorption bands obtained with photoacoustic measurements. The analytical conditions for maximum adsorption of the dyes onto PU foam have been previously studied using the spectrophotometric method and high-performance liquid chromatography (HPLC), but in order to have resolution with HPLC the authors used a buffer solution with pH 7.0 [28]. The present study was performed with buffering at pH 3.0 in order to test the performance of PAS against the FDS technique, since HPLC proved not to function with a buffer solution at pH < 4.5 [13].

B, S and T colorants are characterized by an optical absorption band in the visible part of the electromagnetic spectrum, with high absorptivity. However, the combination of one or more colorants may result in optical absorption bands with partial or total overlapping, which may make it difficult to use spectrophotometric measurements directly for quantitative determination of a colorant. The spectrophotometric absorption spectra of B, S and T dyes in dimethylformamide are shown in Fig. 2. There is clear superposition of the peaks in the range from 350 nm to 550 nm for B, S and T. There is overlapping of almost 100 nm for the S and T spectra. Therefore, if these two components are combined in certain proportions in a specific food, the contribution of each will be difficult to discriminate. A technique detecting pure absorption such as photoacoustic spectroscopy is capable of solving this problem, quantitatively and with a greater limit of detection (LOD). In this study, we are proposing the PAS technique and comparing it with the previously known first derivative technique.

Derivative spectra of the measured spectrophotometric absorption spectra can be generated by mathematical methods. To obtain the derivative at a particular wavelength, by selecting n data points, a polynomial P of degree x is fitted by the least-squares method

$$P_\lambda = a_0 + a_1\lambda + a_2\lambda^2 + \ldots + a_x\lambda^x$$

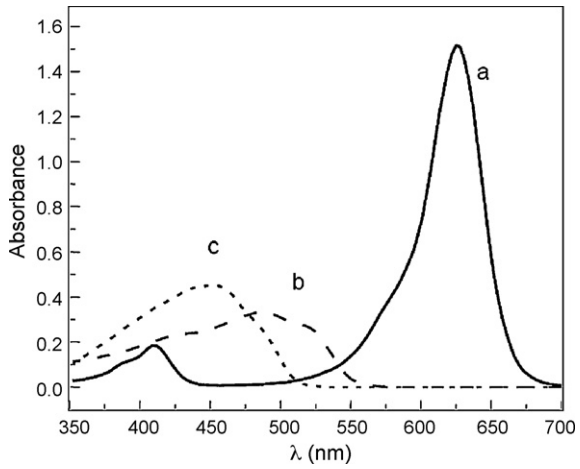

Fig. 2. Spectrophotometric absorption spectra in dimethylformamide ($C = 10\,mg\,L^{-1}$) (a) B, (b) S and (c) T.

and the coefficients at each wavelength are the derivative values, where a_1 is the first derivative, a_2 the second derivative, and so on. Savitzky and Golay [9] developed a very efficient method to perform the calculations; the method also smoothes the data, and this can be used to lessen the decrease in signal/noise ratio. The use of derivative spectra enhances differences among spectra, resolves overlapping bands, and, especially, improves the detectability of the weaker spectral shoulders, and can also be used to reduce the effects of interference from the matrix and/or other absorbing compounds in quantitative analyses [28–31].

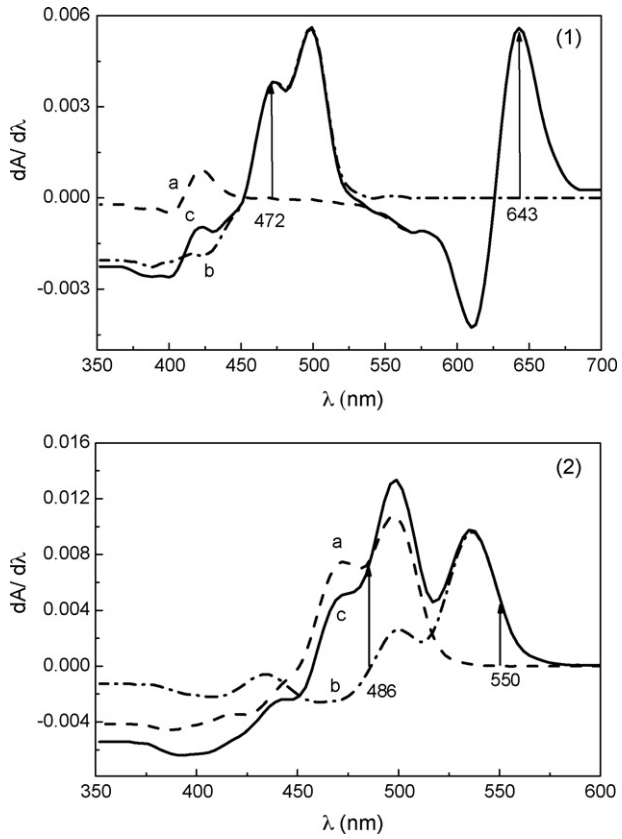

Fig. 3. First derivative spectra of the binary mixtures of food dyes. (1) (a) B ($1.0\,mg\,L^{-1}$), (b) T ($5.0\,mg\,L^{-1}$), (c) B + T mixture. B is determined at 643.0 nm and T is determined at 472.0 nm. (2) (a) S ($10.0\,mg\,L^{-1}$), (b) T ($10.0\,mg\,L^{-1}$), (c) S + T mixture (c). S is determined at 550.0 nm and T is determined at 486.5 nm.

In order to improve accuracy and precision, a number of parameters were studied, including the smoothing function, the zero-crossing wavelengths, and the wavelength interval ($\Delta\lambda$). For the mixtures studied (B + T and S + T), a smoothing function of 11 experimental points and $\Delta\lambda = 3$ nm was chosen. In the first derivative spectrophotometry technique, binary mixtures are investigated by measuring the signal at their zero-crossing wavelength, previously established for each dye in the mixture. The first derivative spectra of the S + T and B + T mixtures are shown in Fig. 3, where the wavelengths used in the analytical measurement are indicated. The calibration graphs, obtained with spectrophotometric signal measurements at the selected wavelengths, were linear up to $1.0\,mg\,L^{-1}$ and the signals produced by each dye were independent of the concentration of the other dye. The limits of detection of each dye for the different binary mixtures analyzed were determined by measuring 10 blanks to obtain a mean and its standard deviation. Detection limits of $0.089\,mg\,L^{-1}$ and $0.56\,mg\,L^{-1}$ were found for S and T, respectively, in the S + T mixture, and of $0.017\,mg\,L^{-1}$ and $0.35\,mg\,L^{-1}$ for B and T, respectively, in the B + T mixture [14,29].

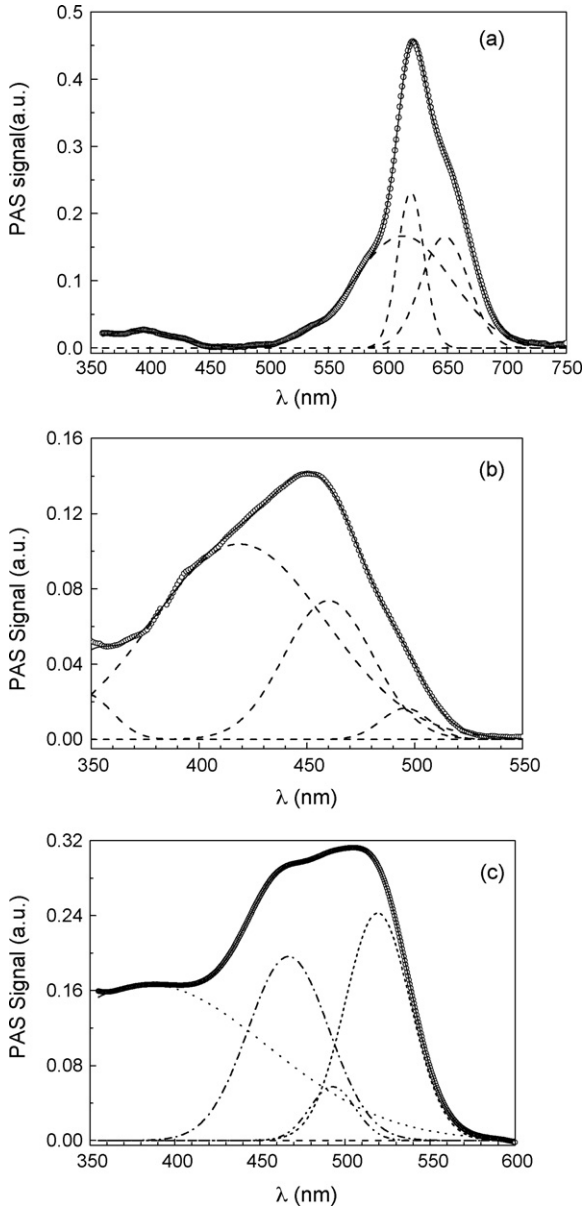

Fig. 4. Spectral de-convolution from Gaussian peaks (photoacoustic spectroscopy) (a) B ($1.0\,mg\,L^{-1}$), (b) T ($1.0\,mg\,L^{-1}$) and (c) S ($1.0\,mg\,L^{-1}$).

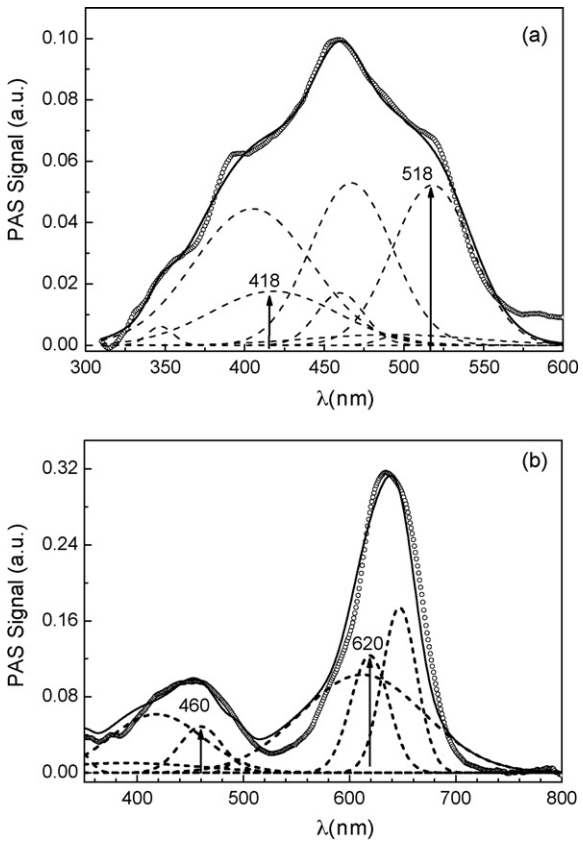

Fig. 5. Spectral de-convolution from Gaussian peaks (photoacoustic spectroscopy) for the binary mixtures (a) S+T mixture (0.2 mg L^{-1}) and (b) B+T mixture (0.5 mg L^{-1}).

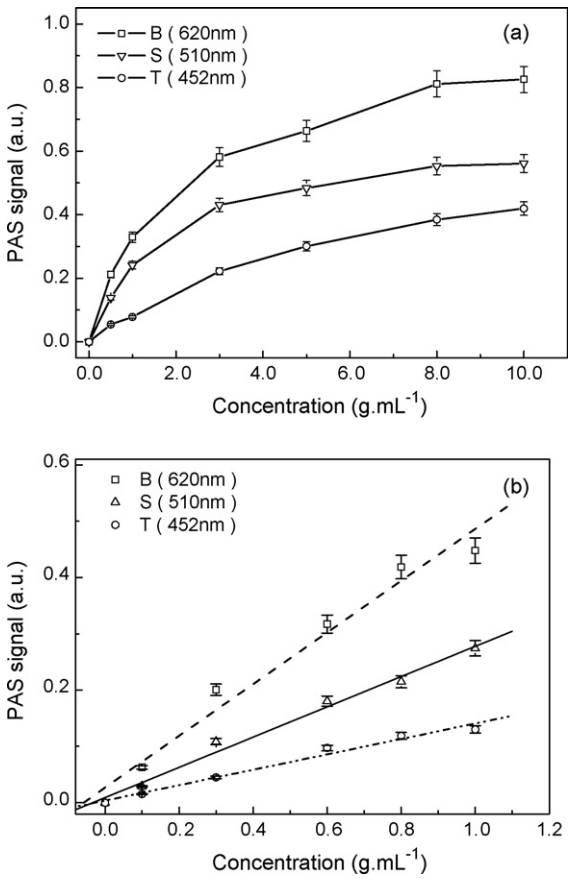

Fig. 6. The calibration curves. PAS maximum band signal as a function of the concentration of each dye, (a) up to 10 mg L^{-1}, and (b) up to 1.0 mg L^{-1}.

PU foam samples with the sorbed dyes (a single dye or a mixture) were investigated using photoacoustic spectroscopy. The photoacoustic spectra of B, S and T and the spectral de-convolution are shown in Fig. 4 (single dyes) and in Fig. 5 (synthetic dye mixtures). The wavelengths for the photoacoustic measurements are shown in the spectra of Fig. 5a at 418 nm and 518 nm, and in Fig. 5b at 460 nm and 620 nm, respectively. Photoacoustic spectra of the single components B, S and T are shown in Fig. 6a and in Fig. 6b, where error bars represent the dispersion. In the first step, the calibration graphs were found to be linear up to 1.0 mg L^{-1}, as shown in Fig. 6b. For concentrations greater than 1.0 mg L^{-1} the photoacoustic response was no longer linear. Therefore, the value of the photoacoustic intensity at the chosen analytical peak (452 nm, 510 nm and 620 nm) follows a monotonic curve with tendency toward a saturated value when the concentration of the colorant exceeds 10.0 mg L^{-1}. Limits of detection of 0.028 mg L^{-1} and 0.086 mg L^{-1} were found for S and T, respectively, in the S+T mixture, and of 0.012 mg L^{-1} and 0.068 mg L^{-1} for B and T, respectively, in the B+T mixture. The results of the quantitative determination for Tartrazine sorbed in PU foam using the PAS method suggest a significant improvement of the limit of detection, when the combination of colorants was investigated and compared against the FDS method.

B, S and T were determined in commercial products (gelatin powder and juice powder), as described in the Section 2. Table 1 shows the dye contents determined by using first derivative spectrophotometry and photoacoustic spectroscopy. A very good agreement was found between the two optical methods. Photoacoustic spectroscopy showed high sensitivity, with a reasonable precision. Although the percentage intrinsic error for all the commercial dyes quantified was small, ~0.3–3.6% for the spectrophotometer results, the PAS method gave errors between ~0.1% and 2.9% (Table 1). The poorest result was that for the colorant S (Sunset Yellow) in the citrus fruits, which was ~2.9%. This result can

Table 1
Dye contents in commercial products (μg g^{-1}) (n = 3).[a]

	First derivative spectrophotometer			Photoacoustic spectroscopy		
	B[b]	S[c]	T[d]	B	S	T
Gelatine powder	–	–	–	–	–	–
Lemon	11.0 ± 0.4	–	98.8 ± 1.4	10.6 ± 0.3	–	101.4 ± 0.1
Peach	–	34.6 ± 0.1	30.0 ± 0.2	–	34.8 ± 0.3	28.7 ± 0.4
Juice powder	–	–	–	–	–	–
Citrus fruits	–	1567 ± 56	874 ± 5	–	1677 ± 49	946 ± 7

[a] Errors refer to three individual analyses.
[b] Brilliant Blue.
[c] Sunset Yellow.
[d] Tartrazine.

be explained by inspection of the individual spectra, since the visible band (PAS results not shown in the present study, see ref. [27]) of T was located between 300 nm and 520 nm, peaking at 460 nm (but the full width at half-maximum FWHM ~120 nm). For the S (Sunset Yellow) colorant, this range was from 300 nm to 580 nm but with two superimposed absorption bands, one near 420 (lower peak) and the other at 520 nm (from 380 nm to 550 nm the total FWHM was ~170 nm). Comparing the spectra of T and S, we found similar color and superposition of their bands, which made it more difficult to quantify them individually for the commercial gelatin powder.

These results indicate that photoacoustic spectroscopy can be used for the simultaneous determination of low concentrations of B, S and T in binary mixtures for control and toxicological studies. As far as we know, PAS has been applied only qualitatively as a method for dyed textile samples and for single-colorant determination in foodstuffs [22,30].

4. Conclusion

Photoacoustic spectroscopy allowed the simultaneous determination of Brilliant Blue, Sunset Yellow and Tartrazine as binary mixtures in gelatin and juice powders, with a very good agreement between the values determined by using first derivative spectrophotometry. Here, in a quantitative study, photoacoustic spectroscopy showed high sensitivity and satisfactory precision, together with its non-destructive character. Although a more rigorous calculation was not carried out for the total error of the PAS method, as a criterion for judging the acceptability of analytical methods [31], these results indicated the potential of photoacoustic spectroscopy as an analytical method in the analysis of food dyes, where no preliminary separation step is required. The goal of the PAS method is the lower deviation, which we quantified as between ~0.1 and 2.9%, slightly smaller than that of the FDS method, which was ~0.3–3.6%.

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