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Photoacoustic Spectroscopy — A New Method for Dye Identification in the Substrate–Dye System

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ABSTRACT

Photoacoustic spectroscopy is a type of absorption spectroscopy and is therefore useful for determining the optical properties of dyed textiles, which depend mainly on the dyes used in the dyeing process. The possibility of applying photoacoustic spectroscopy as an identification method of dyed textile samples is studied using the PES-disperse dyes system. Photoacoustic spectra of the dyed samples have the characteristic shape of the absorption spectra and the results confirm that photoacoustic spectroscopy is a convenient analytical method for dye in the substrate–dye system. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Optical properties of dyed textiles mostly depend on the type and amount of dyes used in the dyeing process. Dyes are organic compounds which selectively absorb visible light in the spectral range of 400–700 nm and they have characteristic spectra.

The optical properties of substrate–dye systems can be investigated through the interaction of electromagnetic waves with matter. Reflection spectroscopy is usually applied for dyestuff identification in textile samples and involves study of the light that is reflected or scattered from the dyed substrate. For dark and saturated colour with very high absorption this method is not convenient because of the weak reflection signals.

Most of the absorbed visible light is, in the nonradiative deexcitation processes, transformed into heat energy. Photoacoustic spectroscopy measures heat production through pressure changes, i.e. sound, and is therefore a type of absorption spectroscopy which offers the ability to measure the absorption spectra of opaque dyed textiles.

The possibility of applying photoacoustic spectroscopy as an identification method of dyed textile samples is here studied on the PES-disperse dyes system. The optical and thermal properties were examined in accordance with the Rosencwaig–Gersho theory.[1] Photoacoustic spectra of primary dyeings and of three-dye combinations were obtained in the spectral range of 400–700 nm and compared with the reflectance and absorption spectra of the same dyestuffs in solution. The results show that photoacoustic spectroscopy is capable of detecting the spectral properties of dyed textiles.

PHOTOACOUSTIC SPECTROSCOPY OF SOLID SAMPLES

Several theoretical models for the photoacoustic effect in solids have been developed.[1–4] The most commonly used is the Rosencwaig–Gersho theory,[1] which is a one-dimensional analysis of the photoacoustic signal in a cylindrical cell consisting of the sample, the gas and the backing material. The sample is illuminated with modulated light. The absorbed light energy is converted into thermal energy and 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 photoacoustic spectrometer is represented in Fig. 1; it consists of a light source, a monochromator, a light modulator (chopper), a photo-

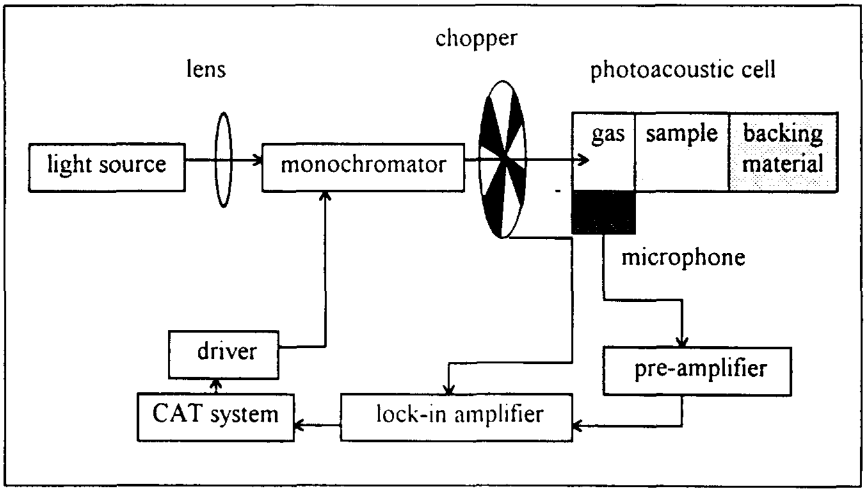

Fig. 1. Typical single-beam photoacoustic spectrometer for solid samples.

acoustic cell with a condenser microphone, a lock-in amplifier and a data acquisition system.

An efficient emitter of light provides strong photoacoustic signals. For determining the optical properties in the visible spectral range (400 –700 nm), xenon or xenon–mercury lamps having 300–1000 W output are usually used. Their corresponding black body temperature is usually between 8000 and 10,000 K. The parabolic reflector and the lens system increases the efficiency of the light source.

The monochromator with grating provides monochromatic light incident to the sample. Its wavelength is determined by the angle between the grating and the light beam. The position of the monochromator is driven by the CAT (computer aided test) system.

Periodic signals (periodic sound pressure variations) are the result of the periodic heating of the sample. The incident light must therefore be intensity modulated and the most common method of modulation used is a mechanical chopper, a rotating plate with holes or slits. Since absorption and heat transfer are linear processes, the frequency of the photoacoustic signal is the same as the chopping frequency. This frequency is usually between 10 and 1000 Hz. The lock-in amplifiers amplify that frequency and raise the signal-to-noise ratio.

The photoacoustic cell consists of a transparent window, a thin layer of air, the sample and the backing material. Walls of the cell are highly reflective and have a high heat capacity, so their temperature is constant. They are made of aluminium or stainless steel.

For detection of photoacoustic signals diaphragm condenser microphones with flat frequency response are most commonly used. Weak acoustic signals are reinforced with a preamplifier.

The photoacoustic signal depends strongly on the intensity of the incident light, which has to be controlled carefully by, for example, alternative measurements of the sample and the reference.

According to Rosencwaig–Gersho theory the photoacoustic signal depends on the optical and thermal properties of the substrate–dye system.

The optical properties of the substrate–dye system are mostly caused by the dyes used in the dyeing process. The incident light is absorbed in the sample according to Lambert–Beer's law. The optical absorption length l_β is defined as follows:

$$l_\beta = 1/\beta = 1/2.303\varepsilon c \qquad (1)$$

where β is the absorption coefficient (cm^{-1}), ε is the molar extinction coefficient ($\mathrm{l\ mol^{-1}\ cm^{-1}}$), and c is the dye concentration in fibres ($\mathrm{mol\ g^{-1}}$).

The heat is transferred through the sample, the backing material and the gas according to their thermal properties, namely thermal conductivity (κ), specific heat (C) and density (ρ). The thickness of the sample, which essentially influences the photoacoustic signal, is defined by the thermal diffusion length μ:

$$\mu = (\kappa/\pi f \rho C)^{1/2} \tag{2}$$

where κ is the thermal conductivity (W m^{-1} K^{-1}), ρ is the density (g cm^{-3}), C is the specific heat (kJ kg^{-1} K^{-1}) and f is the modulation frequency ($\omega = 2\pi$) (s^{-1}).

Only heat generated in the depth μ of the sample contributes to the photoacoustic signal. The amplitude of the thermal wave is attenuated by a factor 1/e when diffusing one diffusion length μ, and by a factor 0.002 by diffusing a length of $2\pi\mu$. The thermal diffusion length μ depends on the chopping frequency.

The relation between the acoustic pressure and the absorption coefficient is rather complicated. Six relatively simple special cases were proposed with the use of reasonable approximations. The cases are grouped by the relation among the thermal diffusion length μ, the optical absorption length l_β and the length of sample 1. The cases are graphically represented in Fig. 2.

Optically transparent samples have a much longer optical absorption length l_β than the length of the sample ($l_\beta >> 1$). The light is absorbed throughout the length of the sample and some light is transmitted through

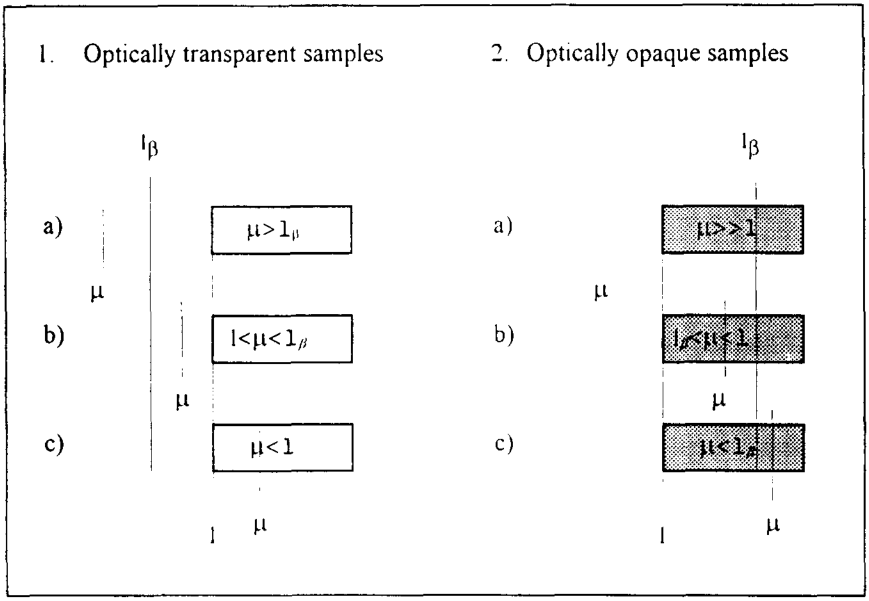

Fig. 2. Special cases in the Rosencwaig–Gersho theory — the light comes from the right-hand-side.

the sample. If the thermal diffusion length is longer than the length of the sample (cases 1a and b, Fig. 2), the signal is proportional to the absorption coefficient, inversely proportional to the modulation frequency, and depends on the thermal properties of the backing material. If the thermal diffusion length is much shorter than the length of the sample (case 1c), the signal is proportional to the absorption coefficient, $\omega^{-3/2}$ and the thermal properties of the sample.

Optically opaque samples ($l_\beta < 1$) absorb all the incident light. If the thermal diffusion length μ is longer than the optical absorption length l_β (cases 2a and b), the signal is saturated and simply proportional to the energy absorbed by the sample. The microphone detects the power spectrum of the incident light. The signal is independent of the optical absorption coefficient and proportional to ω^{-1}. By increasing the modulation frequency the thermal diffusion length μ is decreased. In case 2c the thermal diffusion length μ is much shorter than the optical absorption length l_β; the signal is therefore weaker but proportional to the absorption coefficient β and $\omega^{-3/2}$.

EXPERIMENTAL

Substrate

Textured woven polyester fabric was used as a substrate (Table 1).

The fabric was thermofixed and bleached with FWA (fluorescent whitening agent).

Sample dyeing

The following dyestuffs were used: C.I. Disperse Yellow 198, C.I. Disperse Red 92 and C.I. Disperse Blue 56. The substrate was dyed with various

TABLE 1
Technical Data for PES Fabric

Filament density at 23°C (g cm^{-3})		1.379
Filament number (tex)	warp	5/36/200
	weft	5/36/0
Structure:		atlas
No. of threads per cm	warp:	81
	weft:	42
Weight (g m^{-2})		74.3
Thickness at pressure 2 kPa (mm)		0.251
Fabric density ρ_t (g cm^{-3})		0.296
Thermal conductivity κ (W m^{-1} K^{-1})		0.0944
Specific heat C_t (kJ kg^{-1} K^{-1})		1.064

concentrations of each dyestuff (as a percentage of the weight of the fabric): 0.05%, 0.1%, 0.5%, 1%, 1.5%, 2%, 2.5%, 3% and with different three-dye combinations. The dyeings were performed by the HT exhaustion dyeing process (at 130°C) according to dyeproducer procedure, using a laboratory machine Labomat-BFA (W. Mathis), which ensures optimal and reproductive dyeing conditions.

Thermal and optical properties of the PES substrate–disperse dye system

Thermal properties are defined by the thermal diffusion length μ [eqn (2)] which is, for the chosen substrate, at modulation frequency $f = 130\ \mathrm{s}^{-1}$ equal to:

$$\mu = 27 \mu\mathrm{m}$$

Only heat originated at the depth of 27 μm can diffuse from the sample to the border field of the air and thus cause the acoustic signal. At the fixed modulation frequency f the thermal diffusion length μ is the constant of the specific substrate.

Optical properties are defined by optical absorption length l_β, which depends on the type and concentrations of the dyes used for dyeing [see eqn (1)].

For estimating the molar extinction coefficient ε, the commercial dyestuffs were previously purified and dissolved in a mixture of dimethylformamide and water (ratio 19:1) with the addition of 2% glacial acetic acid. The absorbance of dye solutions (1×10^{-5}, 2×10^{-5}, 3×10^{-5}, 4×10^{-5}, 5×10^{-5}, 6×10^{-5} and 8×10^{-5} mol liter^{-1}) was measured at maximal absorption wavelength and the molar absorbance coefficient ϵ was calculated according to the Lambert–Beer law.

The optical absorption length l_β of a specific dye in the substrate has the lowest value at a higher dye concentration due to light absorption. The dye concentration in fibers depends on dye exhaustion from the dyebath and on the amount of pure dye in a commercial product. Samples dyed with 3% of dyestuffs were extracted, and the dye concentration in the fibers were estimated according to the Lambert–Beer law.

The calculated values for optical absorption length l_β [eqn (1)] for 3% dyeings with the disperse dyes used were in the range 0.8650–1.3119 cm.

According to the experimentally determined values for μ and l_β, the analysed system (PES–disperse dyes) corresponds to the Rosencwaig–Gersho special case 1c, because the following criteria are fulfilled:

$l_\beta > 1$, $8650\ \mu\mathrm{m} - 13{,}119\ \mu\mathrm{m} > 251\ \mu\mathrm{m}$
$\mu < 1$, $27\ \mu\mathrm{m} < 251\ \mu\mathrm{m}$
$\mu < l_\beta$, $27\ \mu\mathrm{m} < 8650\ \mu\mathrm{m} - 13{,}119\ \mu\mathrm{m}$

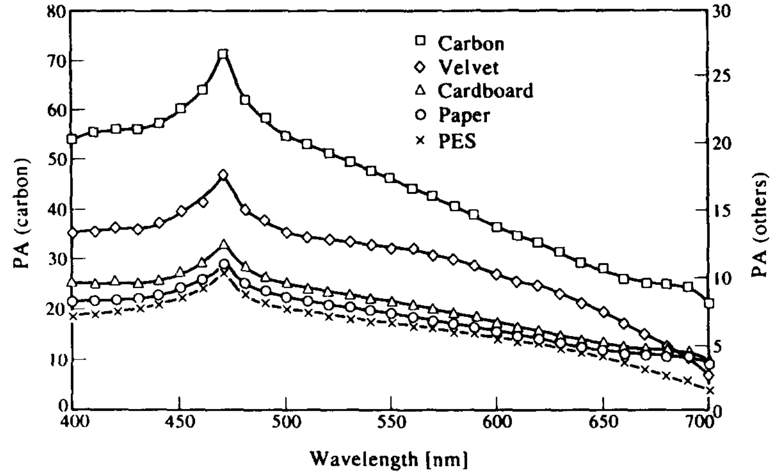

Fig. 3. Photoacoustic spectra of different black materials.

Transmittance measurement

For transmittance measurement the disperse dyes were dissolved in a solution of dimethylformamide + water (19:1) + 2% glacial acetic acid. The measurements were carried out using a Lambda 2 UV-VIS spectrophotometer (Perkin-Elmer) in the visible range 400–700 nm at 1 nm intervals.

Photoacoustic measurement

The photoacoustic spectrometer used in this work was constructed at DTNW (Deutsches Textilforschungszentrum Nord West), Krefeld, Germany.[5] Photoacoustic measurements of dyed samples were obtained at a constant modulation frequency of 130 Hz in the visible range from 400 to 700 nm at 10 nm intervals. As an absolute black standard acetylene carbon on silica glass is usually used. The photoacoustic spectrum of this carbon (Fig. 3) shows the construction characteristic of the spectrometer. Maximal amplitude value at $\lambda = 470$ nm is due to the use of the xenon lamp, the decrease of amplitude values with increasing wavelength is due to the angular reflectivity of the monochromator. Therefore, all spectra must be normalized against the black standard to eliminate the construction characteristics of the spectrometer.

The black standard prepared in this way is very sensitive to scratching and not suitable for permanent use and, therefore, a more adequate reference black standard was selected. Various black materials were tested (black paper, black cardboard, black velvet, black dyed PES fabric). Due to the best fit of the black paper spectrum to the carbon spectrum, and the best repeatability of results over a long period of time, black paper was found to be the most adequate reference standard. As black paper is not 'absolute black', the amplitude values of the black paper were normalized with the amplitude values of black carbon, which represents the correction factor.

The samples were measured alternately with the reference black standard (black paper). All spectra were normalized against the reference black standard and were corrected with the correction factor of carbon.

Reflectance measurement

The reflectance spectra of dyed PES samples were obtained using a Spectro Sensor II reflectance spectrophotometer (ACS) in the range 400–700 nm at 10 nm intervals. No comparison was made between the photoacoustic spectrum and the log of the reflectance spectrum, since the objective of the overall investigation was to evaluate the possibility of applying the photoacoustic amplitude values, instead of reflectance values, in computer match predictions. Results of this will be reported later.

RESULTS AND DISCUSSION

Figure 4 shows the absorption spectra of various disperse dye solutions at a concentration of 1×10^{-5} mol liter^{-1} and 4×10^{-5} mol liter^{-1}. The absorption values were calculated from measured transmittance values T as $(1-T)$. Each dye has a characteristic absorption curve with an absorption maximum at a fixed wavelength, namely C.I. Disperse Yellow 198 at 436 nm, C.I. Disperse Red 92 at 523 nm and C.I. Disperse Blue 56 at 636 nm.

The photoacoustic spectra of dyed PES samples with selected disperse dyes at a concentration of 0.5 and 3% are shown in Fig. 5. They have a similar shape to the absorption spectra, but absorption maxima are less distinctive. The main difference appeared in the spectral range of 400–450 nm due to the FWA (fluorescent whitening agent) used for the PES bleaching. A sample containing a fluorescent compound absorbs, in addition to UV light, light at the shorter wavelength region of the visible spectrum, and thus contributes to the photoacoustic signals.

As a comparison to the photoacoustic spectra, the reflectance spectra of the same dyed samples are shown in Fig. 6. Dyed samples with 3% of the dyestuff are dark and saturated and the reflections signals are weak in the absorption maximum band. Therefore, the absorption maxima are far less distinct than they are in photoacoustic spectra. Because the samples are, during the measurement, illuminated with polychromatic daylight which also contains UV light, the fluorescence affects the reflectance spectra especially at lower dyestuff concentrations.

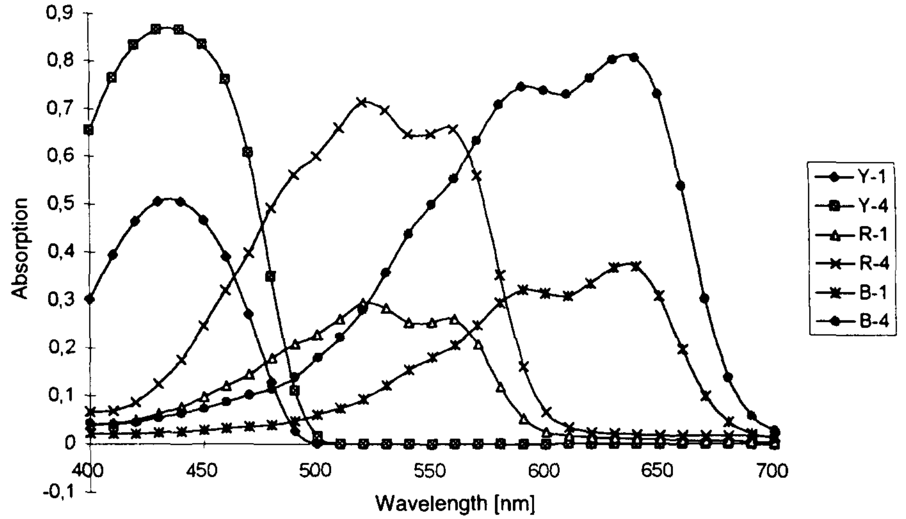

Fig. 4. The absorption spectra of various disperse dye solutions. Y, Yellow; R, red; B, blue; 1, 1×10^{-5} mol liter^{-1}; 4, 4×10^{-5} mol liter^{-1}.

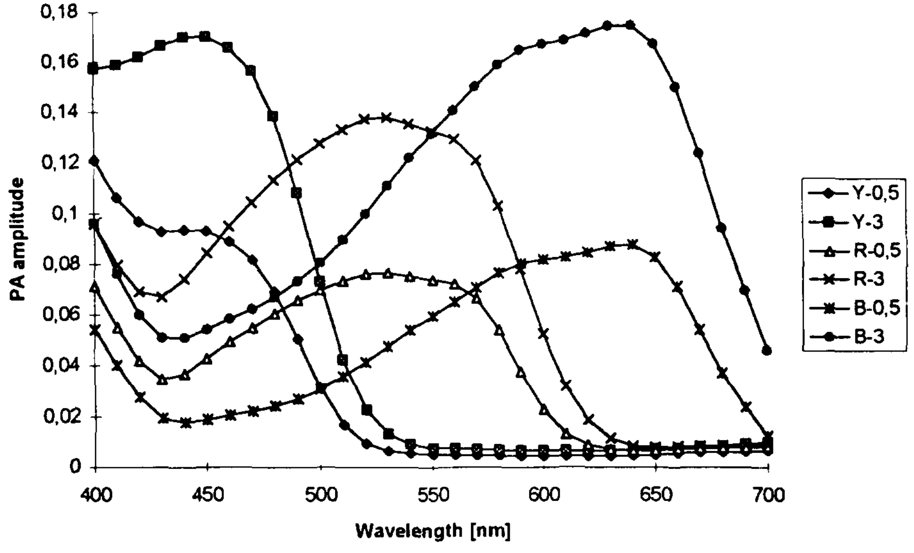

Fig. 5. The photoacoustic spectra of dyed PES samples with various disperse dyes. Y, Yellow; R, red; B, blue; 0.5, 0.5% OWF; 3, 3% OWF.

Photoacoustic spectra of primary dyeings with C.I. Disperse Red 92 are displayed in Fig. 7. At an increased dye concentration in PES fibres the photoacoustic amplitude increases, but the shape of the spectra remain

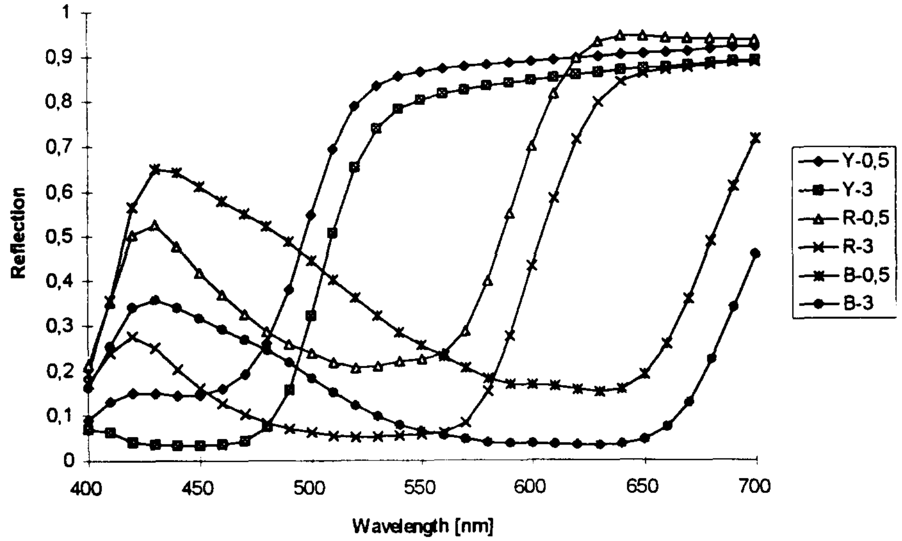

Fig. 6. The reflectance spectra of dyed PES samples with various disperse dyes. Y, Yellow; R, red; B, blue; 0.5, 0.5% OWF; 3, 3% OWF.

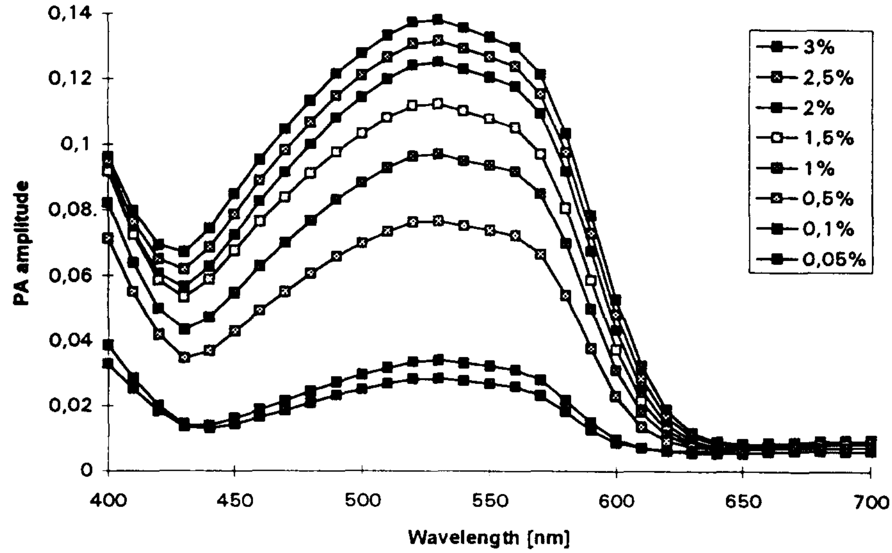

Fig. 7. Photoacoustic spectra of primary dyeing with C.I. Disperse Red 92.

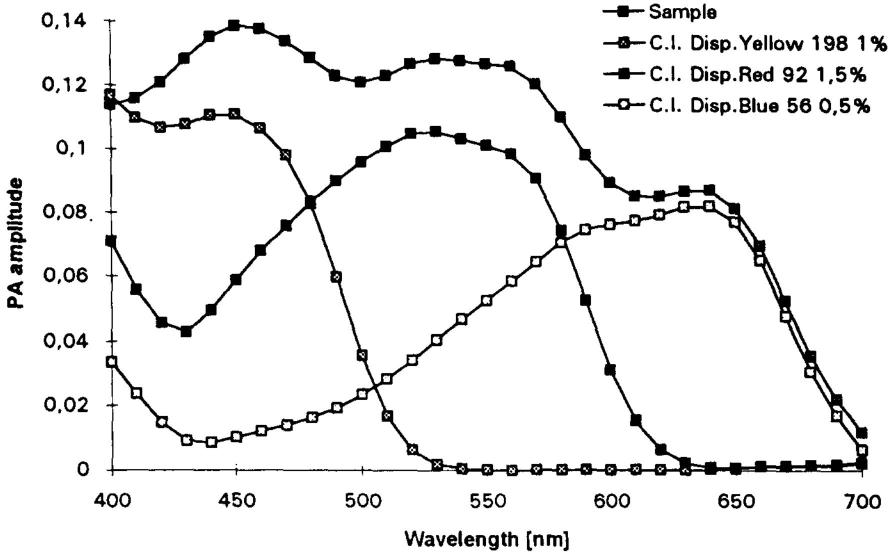

Fig. 8. Photoacoustic spectra of the three-dye combination sample with individual dyes.

similar even at higher dyestuff concentrations, and do not overlap in the absorption maximum band as the reflectance spectra do.

Figure 8 shows photoacoustic spectra of three-dye combination samples and of each individual dye in the combination. The absorption maxima of the individual dye corresponds well to the absorption maxima of the sample.

CONCLUSION

The possibility of applying photoacoustic spectroscopy as a method for dye identification in the substrate–dye system was studied using PES fabric disperse dyes. Experimentally determined optical and thermal properties of the PES disperse dye system correspond to the Rosencwaig–Gersho special case 1c. This means that:

(1) the photoacoustic signals are proportional to the absorption coefficient β and, respectively, to the dye concentration in PES fibers,

(2) only heat generated one thermal diffusion length μ from the sample surface caused the photoacoustic signals,

(3) light absorption over distances which are longer than the thermal diffusion length μ does not influence the measurement results.

Based on the photoacoustic spectra of the dyed samples used in this investigation, we can conclude that photoacoustic spectroscopy is a convenient method for dyestuff identification in textiles.

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