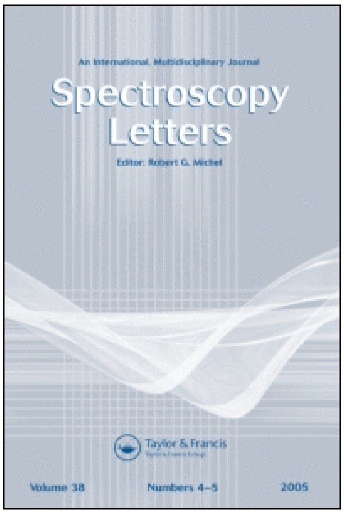

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PHOTOACOUSTIC SPECTROSCOPIC STUDIES OF INKS

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PHOTOACOUSTIC SPECTROSCOPIC STUDIES OF INKS

Key Words: Photoacoustic Spectroscopy, Absorption spectroscopy, Inks

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ABSTRACT

Photoacoustic spectra of some sketch pen and fountain pen inks of different makes and colours, and a correcting fluid (used in cyclostyling) have been recorded in the spectral range of 350 to 750 nm, at room temperature of 25 °C. The spectra have been analyzed in order to compare the nature of different inks. For this study, an open photoacoustic cell with PZT transducer having obvious advantages over gas phase microphone detection system, has been used.

INTRODUCTION

Photoacoustic (PA) spectroscopy using a gas phase microphone detection system is being widely employed[1-4] for the study of various samples in comparison to the conventional transmission/reflection spectroscopy. But, in such detection system also, the PA signal gets affected by external noise in less absorbing samples and gets saturated in highly absorbing samples. In order to overcome these difficulties, PZT transducer[5-7] has been used in place of microphone, for liquid samples. The advantages of a PZT transducer over a microphone are: (i) the PA signal is unaffected by the external acoustical noise and (ii) the PA signal does not get saturated because of its response in wide frequency range. An open PA cell with PZT transducer was invented and used by Helander[7,8] to study absorption spectra of a number of liquids such as dye solutions including black ink[8] etc. The cell of this design has been employed by us to measure PA absorption spectra of laser dyes in solution form[9] and of some commercial inks[10]. In the present study we have extended our previous studies[10] and have tried to find the wavelength position of absorption peaks, observed in the PA spectra of some sketch pen and fountain pen inks and a correcting fluid. The PA spectra of these samples have been compared with the absorption spectra obtained by conventional transmission spectroscopic technique and the results thus obtained have been correlated with those reported in the literature[11,12]. It has been found that the PA spectra show better resolution.

EXPERIMENTAL PROCEDURE

PA spectra of sketch pen inks of two colours (make-A), fountain pen inks of four colours (make-B), fountain pen inks of four colours (make-C) and a correcting fluid (used in cyclostyling) have been recorded on a PA spectrophotometer[9], at a room temperature of 25 °C. The experimental set-up and conditions were the same as described in our earlier work[9,10].

The samples of inks of different colours and makes were procured from the local market as per their availability. A quantity of 0.5 cc of each ink was sufficient to fill the sample cavity. The modulation frequency of the radiation was kept at 12 Hz with a time constant of 10 seconds and the scan speed of monochromator at 20 nm/minute. Before replacing the other samples, the sample cavity was thoroughly cleaned each time. The records of PA spectra on each sample were repeated at least ten times in order to ascertain the reproducibility and was found to be within experimental constraints. But incase

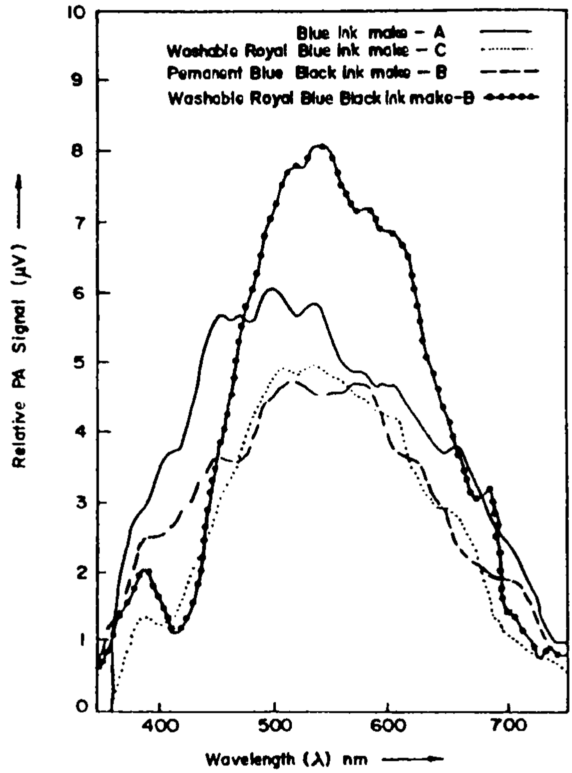

Fig. 1 **Photoacoustic spectra of sketch pen Blue ink make-A; and fountain pen inks: Washable Royal Blue make-C, Permanent Blue- Black make-B and Washable royal Blue-Black make-B.**

of correcting fluid, the sample had started drying to form a semisolid and then to solid even during the second scan. Consequently, the PA signal generated due to absorption in the sample could not be recorded. The PA spectra thus recorded in the spectral range of 350 to 750 nm are shown in Figs. 1 to 3. The absorption spectra of the above mentioned samples were also recorded on a CARY-17D spectrophotometer for comparative study and are shown in Figs. 4 to 6.

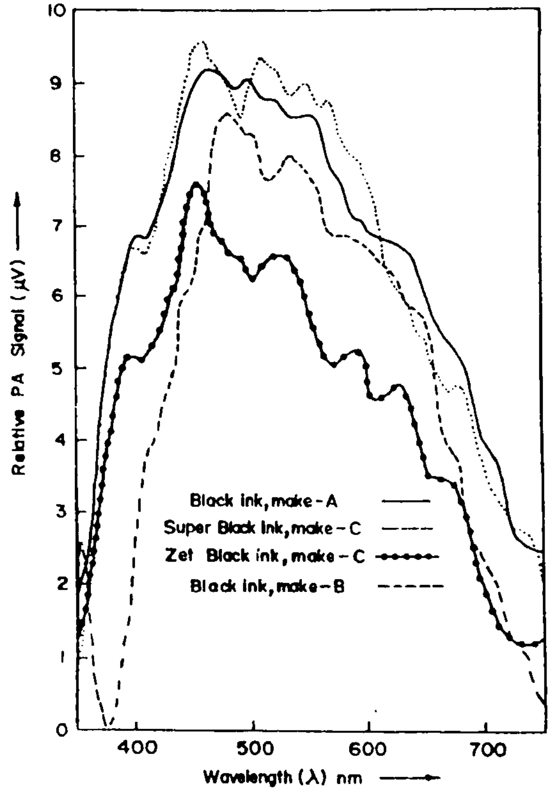

Fig. 2 Photoacoustic spectra of sketch pen Black ink make-A; and fountain pen inks: Super Black make-C, Zet Black make-C and Black make-B.

RESULTS AND DISCUSSION

While Figs. 1 and 2 show a group of PA spectra of blue and black inks respectively, Fig. 3 shows a group of PA spectra of correcting fluid, master brown and permanent turquoise inks. In each figure, PA spectrum covering the absorption in nearly the same spectral region have been grouped together.

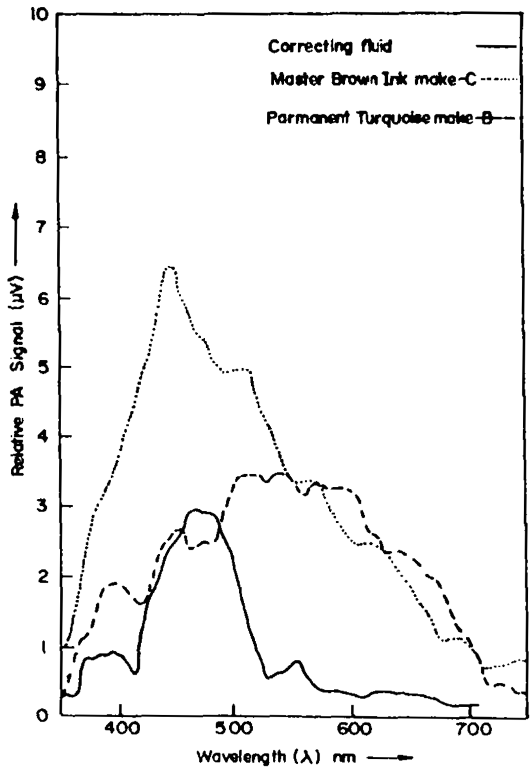

Fig. 3 **Photoacoustic spectra of Correcting Fluid and fountain pen inks: Master Brown make-C and Permanent Turquoise ink make-B.**

However, because of variation in their characteristic absorption, there is slight variation in their absorption maxima.

The PA spectra of blue and black inks of make-B, reported earlier[11] by using closed PA cell and microphone, match with their corresponding spectra recorded presently. The PA spectra of inks (Fig. 1 to 3) show a correspondence with the spectra of inks or pigments of the same colour reported by conventional

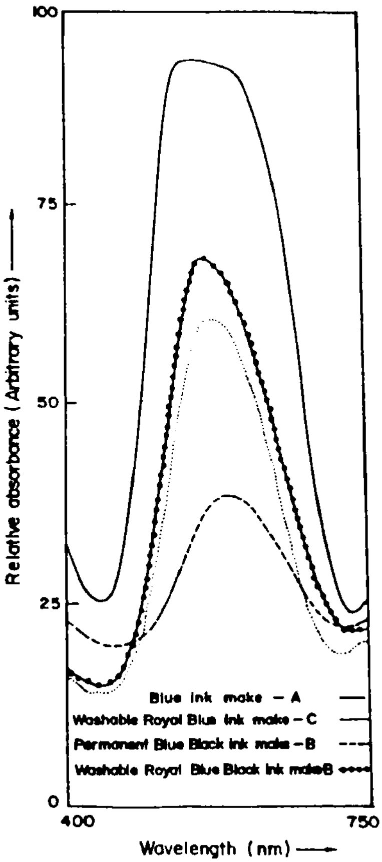

Fig. 4 Absorption spectra of sketch pen Blue ink make-A; and fountain pen inks: Washable Royal Blue make-C, Permanent Blue- Black make-B and Washable royal Blue-Black make-B.

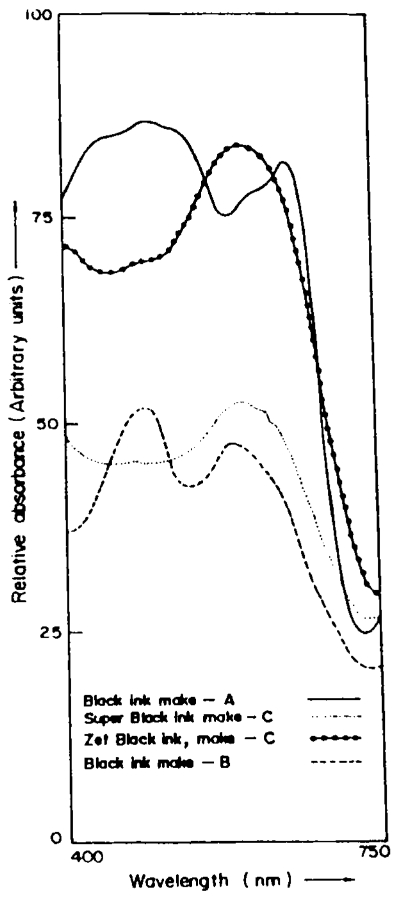

Fig. 5 Absorption spectra of sketch pen Black ink make-A; and fountain pen inks: Super Black make-C, Zet Black make-C and Black make-B.

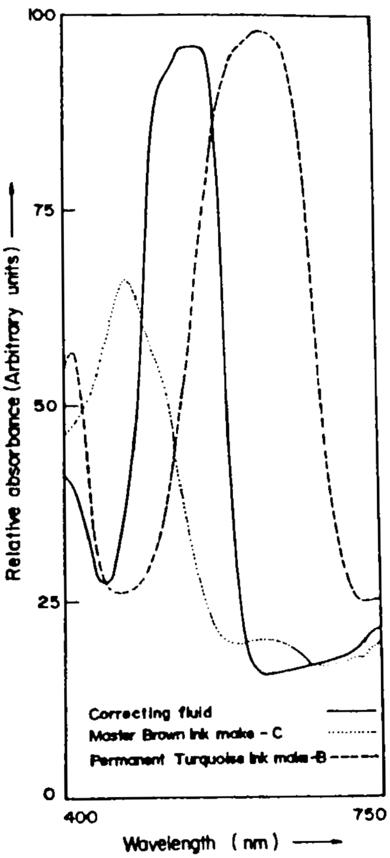

Fig. 6 Absorption spectra of Correcting Fluid and fountain pen inks: Master Brown make-C and Permanent Turquoise ink make-B.

technique of reflectance spectroscopy[12-14] and with their absorption spectra recorded presently on CARY-17D spectrophotometer (Figs. 4 to 6).

Any variation in the absorption spectra (Figs. 4 to 6) from the corresponding PA spectra of inks (Figs. 1 to 3) may be attributed to the sample preparation as for example, for recording absorption spectra by CARY-17D, the sample needs dilution or concentration, as the case may be, to get a reasonable spectra. The comparison of Fig. 3 with Fig. 6 show a large variation in the two spectra of the same sample and it is because of compositional degradation during scan and the period of scan in the two cases. It is worth pointing out that in case of PA spectra the scanning speed of monochromator was low and the sample was drying fast whereas the scanning speed was fast in case of spectra recorded on CARY-17D.

The PA spectra of different inks show many absorption peaks, shoulders and tendency to form peaks. These absorption features might be due to the presence of pigments and their vehicle liquids in the solution of inks. The wavelength of the few prominent peaks of different inks are given in Table I. The position of the λ_{max} is also shown by the mark "*". In comparison to PA spectra of inks, the conventional absorption spectra, recorded on CARY-17D, do not show such absorption features. It shows that the PA spectroscopy using PZT open cell has better resolution. The practical application of these peak positions can be utilized for the forensic applications. Because of the trade secret, the manufacturers do not disclose the name of the pigments used in the particular ink, however, the position of these absorption peaks may be used for the identification of the pigments.

CONCLUSIONS

Spectrophotometry is of great importance in the dye industry for purposes of identification and assessment. Further, testing of both raw materials and finished inks is of importance in order to secure uniformity and standard quality. In case of conventional transmittance technique, the nature of sample gets affected

Table I

Trade Name, Make, Colour and position of Prominent Photoacoustic absorption peaks for 10 inks and a correcting fluid

Sample No.	Trade Name	Make	Prominent PA absorption peaks (nm)
1.	Washable Royal Blue Black	B	387.8, 519.7, 542.4*, 583.3, 601.5, 686.3, 704.5, 737.8
2.	Permanent Blue Black	B	389.4, 450.0, 492.6, 516.6*, 572.7, 622.7, 643.9, 704.5
3.	Washable Royal Blue	C	386.4, 509.1, 534.8*, 580.3, 604.5, 643.9, 692.4
4.	Blue	A	383.3, 410.6, 453.0, 469.7, 498.5*, 536.4, 575.7, 592.4, 601.5, 656.1
5.	Black	B	354.6, 442.3, 479.2*, 500.4, 534.6, 580.7, 629.9, 688.4, 726.9
6.	Zet Black	C	393.1, 451.5*, 485.4, 525.4, 589.9, 626.9, 663.8
7.	Super Black	C	396.1, 457.7*, 509.9, 546.9, 565.4, 586.9, 676.1, 728.5
8.	Black	A	403.8, 462.3*, 497.7, 519.2, 551.5, 593.1, 629.9, 703.8
9.	Permanent Turquoise	B	368.3, 394.3, 447.7, 472.1, 508.7*, 537.8, 566.8, 597.3, 621.7, 725.6
10.	Master Brown	C	383.3, 444.6*, 470.6, 510.3, 566.8, 612.6, 688.9, 743.9
11.	Correcting Fluid (Cyclostyling)	D	353.0, 368.3, 382.1, 392.7, 447.7, 466.3*, 481.3, 551.5, 586.6, 618.7

* marks the position of λ_{max}

due to dilution while in case of reflectance spectroscopy, the properties of base material dominates. However, the present study shows that PZT - PA spectroscopy is a quick, direct and accurate technique for identification and assessment of the quality of inks.

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