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Some Special Observations Regarding Visible Transmission Spectra of Inks and an Improved Method for Their Discrimination by Microspectrophotometry

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ABSTRACT: Various blue and black inks are shown to change their transmission spectra by applying pressure and smearing them as deposits on glass slides. A similar phenomenon is observed with deposits of copper phthalocyanine tetrasulfonic acid tetra sodium salt. It is shown that transmission spectra of small samples of inked paper fibers smeared (crushed) on glass slides resemble spectra of smeared ink deposits and are more reproducible than spectra of inked fibers in a mounting medium. This advantage is especially significant in the case of examining ink traces on tinted paper.

KEYWORDS: questioned documents, inks, spectroscopic analysis, microspectrophotometry

It was shown that spectra of inks on paper deviate from the Beer-Lambert law as a result of scattering and variations in the opacity of the paper in the transmission and the reflectance modes and also as a result of bronzing in the reflectance mode [*1*]. To obtain best reproducibility (consistent with the Beer-Lambert law), a transmission microspectrophotometry of small samples of ink stained paper fibers in mounting medium has been recommended [*1–4*]. However, even using this method, the reproducibility may be quite poor when the ink strokes are on tinted paper [*1*]. It was reported also that poor reproducibility was obtained for black inks strokes from roller ball and from porous tip pens on good quality paper [*5*].

In this work we studied the effect of smearing (crushing) of inked paper fibers (while applying pressure) and ink deposits (on glass slides) on the transmission spectra and their reproducibility in comparison with the spectra of unsmeared ink deposits.

Experimental Procedure

Instrumentation

The system used was the Docuspec TM/1 computerized microspectrophotometer (Nanometrics, Inc.) which includes Olympus BHT microscope with quartz halogen lamps. The instrument is equipped with a variable measuring aperture, and its wavelength range

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is from 380 to 764 nm. The software normalizes the unknown spectrum before its comparison to standards in the memory [*1*]. The degree of similarity in color of the unknown and the standard is reported as a match number (m.n.) that ranges from 0.00 (no difference) to 100 maximum difference.

Sample Preparation Processing and Measurement of Spectra

Ten blue and ten black (ballpoint, roller ball, and fiber tip) pens (Table 1) were examined in this study. All the pen inks were deposited on glass slides by writing directly on glass slides or making many strokes with a pen on a polyethylene plastic sheet and pressing it on a slide [*1*]. Smearing of these inks' deposit using an engraving tool (Fig. 1) having about 1-mm-diameter ball was carried out by following method. While observing the ink deposit through a stereomicroscope, the tool was applied with pressure on a small area moving and rolling it in a random manner. For examination of inked traces on paper, a small area of inked fibers was transferred on a slide and then smeared (crushed) using the engraving tool or immersed in a mounting medium [*1*] (Permount®, Fisher Scientific Company). Various degrees of pressure were applied while smearing, however, not too great to break the glass slides.

A ×20 objective lens was used to record spectra and the measurement area was usually approximately 20 by 40 μm. For each ink, an area was selected to give maximum absorbance in the range of 0.5 to 1.5 optical density (O.D.) and the spectrum obtained was stored as a standard in a memory. Subsequently spectra were recorded from five varying areas of the same ink deposit to cover a large absorbance range and were compared to the standard using the Docuspec software. Spectra of smeared ink deposits were compared with those of unsmeared ones of the same ink and also with the smeared and mounted inked fibers.

The possible influence of the type of the paper on the spectra obtained was examined for all inks in this study by comparing their spectra on a brown cover paper to those on a white paper. A brown cover paper was chosen for the comparison because of its relatively high and variable absorbance.

The most popular dyes in modern glycol-based inks are the blues based on the compound copper phthalocyanine. These dyes are prepared by sulfonating or chlorosulfonating copper phthalocyanine pigment and reacting the sulfonic acids with amines to form colored sulfonic acid salts or sulfonamides [*6*]. Since variations were observed in spectra

TABLE 1—*Pens used in the study.*

Blue	Black
1. Parker Medium	Pelican roller
2. Exact Lamy	Parker roller
3. Pelican	Schwan-stabilopoint 88
4. Parker roller ball floating ball	Stick 433
5. Starlet	Paper Mate Medium
6. Sonator	Ballograph Epoca
7. Pilot Hi-Tecpoint	Pilot Hi-Tecpoint
8. Stick 433	Unix Swiss
9. Donni M	Inoxcrom black
10. Universal	Mont Blanc Quick, pen medium

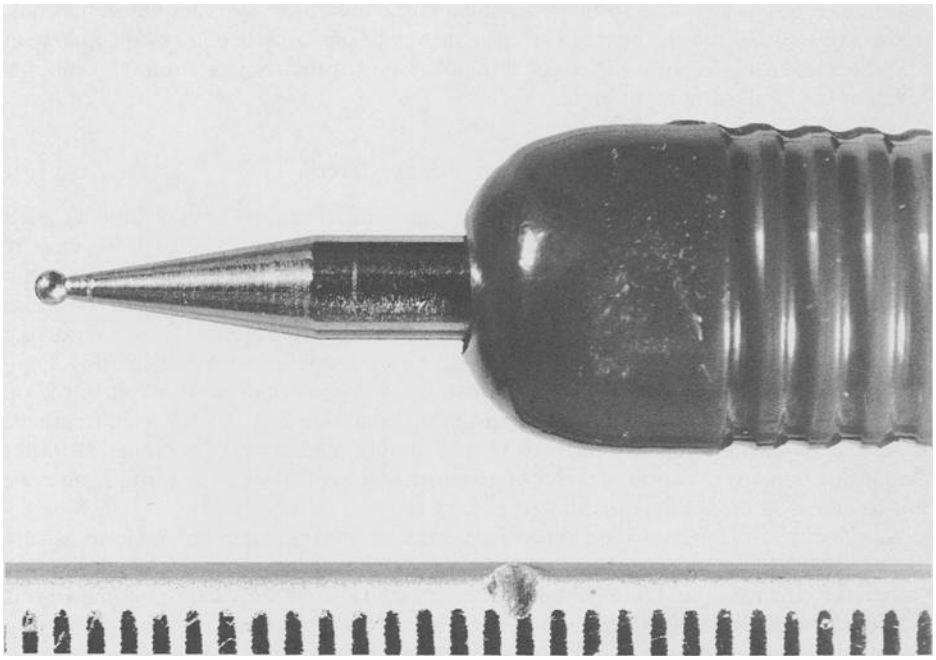

FIG. 1—*Tip of the engraving tool (every division in the scale = 1 mm).*

of some inks upon smearing their deposits while applying pressure, and inks are complex formulation of dyes and other ingredients, it was interesting to examine the effect of pressure and smearing on single-component dyes.

Copper phthalocyanine tetrasulfonic acid tetrasodium salt and copper phthalocyanine were chosen to study the effect of smearing while applying pressure on their transmission spectra. The two copper compounds were purchased from Aldrich Chemical Company, Inc., Milwaukee, Wisconsin.

The salt dye was dissolved in water, deposited on the glass slide, and dried. The smearing of the deposit was carried out in the same manner as in the case of inks. Copper phthalocyanine is practically not soluble in most of the solvents [7]. Since the pigment is quite soft, it was placed on the glass slide and smeared with various degrees of pressure (beginning from very light pressure). The transmission spectra were recorded as a function of various degrees of pressure.

It was interesting to study whether changes in visible transmission spectra are accompanied by changes in crystallographic structures as may be reflected by X-ray diffraction pattern. The possible effect was studied in the case of the two aforementioned copper compounds.

Analyses were carried out with a microprocessor-controlled Diano 8000 instrument. A standard copper target tube (wavelength = 0.154 15 nm) with a nickel filter was used. The diffractograms were registered by recorder. The instrumental conditions are as follows: voltage, 40 kv; current, 25 mA; range, 1000 counts/s; time constant, 2.5 s; and scan rate, 2/min.

The samples were prepared in two ways:

(*a*) the pertinex holder (dimensions of cavity: 25 by 14 by 1 mm) was filled with unground or ground copper compounds.

(*b*) circular pellets of 0.5-in. (1.3-cm) diameter of the copper compounds, having thickness about 1 mm, were prepared in a press (for preparing KBr pellets for I.R analysis) using 50 ton force.

Results and Discussion

All the examined blue and black inks in this study practically obeyed the Beer-Lambert law (good reproducibility) when their traces on white or brown paper were smeared (while applying pressure) on glass slides. The spectra reproducibility obtained by method of mounting inked fibers in Permount was significantly less, especially in the case of black inks on white or brown paper and in the case of blue inks on brown paper (Table 2).

Figures 2 to 5 demonstrate the better reproducibility obtained in spectra obtained by smearing the ink traces on brown papers in comparison to mounting them in Permount.

TABLE 2—*Spectra reproducibility of inks obtained by smearing and mounting methods.*

	Smearing Method		Mounting Method	
	Average m.n.		Average m.n.	
	White Paper	Brown Paper	White Paper	Brown Paper
Blue inks	0.03 + 0.02	0.06 + 0.03	0.05 + 0.01	0.27 + 0.2
Black inks	0.03 + 0.03	0.05 + 0.03	0.11 + 0.05	0.21 + 0.06

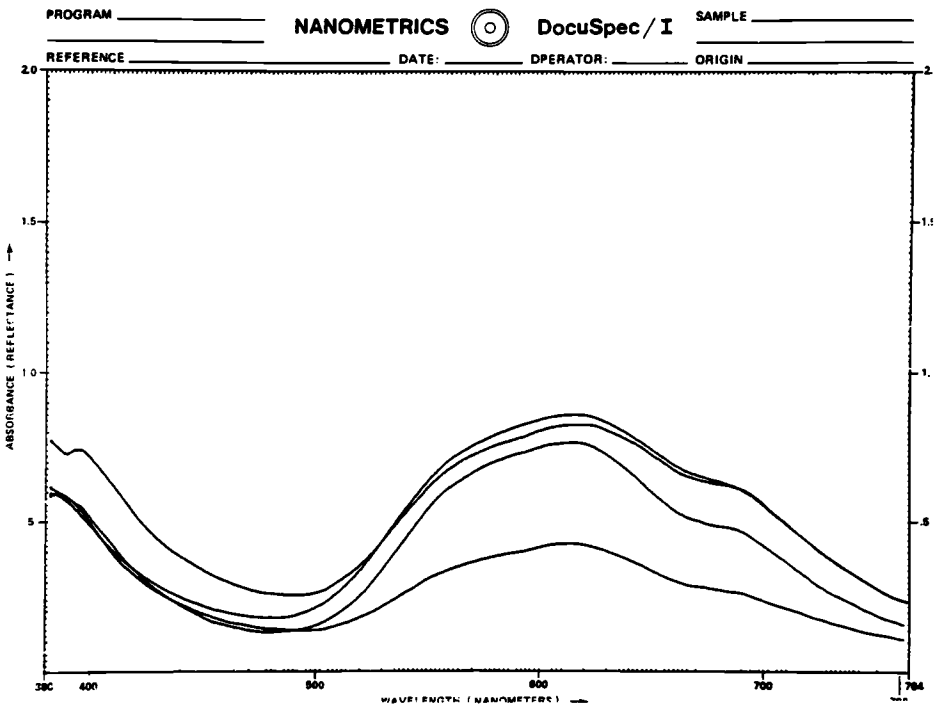

FIG. 2—*Transmission spectra of the inked (blue Parker floating ballpoint pen ink) brown paper fibers in Permount.*

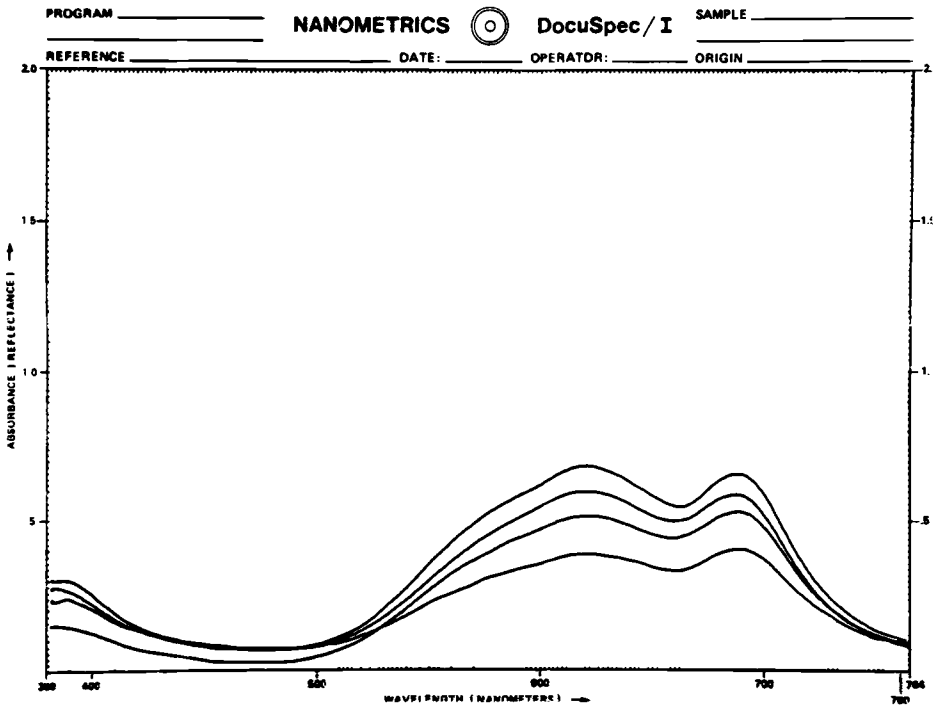

FIG. 3—*Transmission spectra of smeared inked brown paper fibers (the same ink as in Fig. 2).*

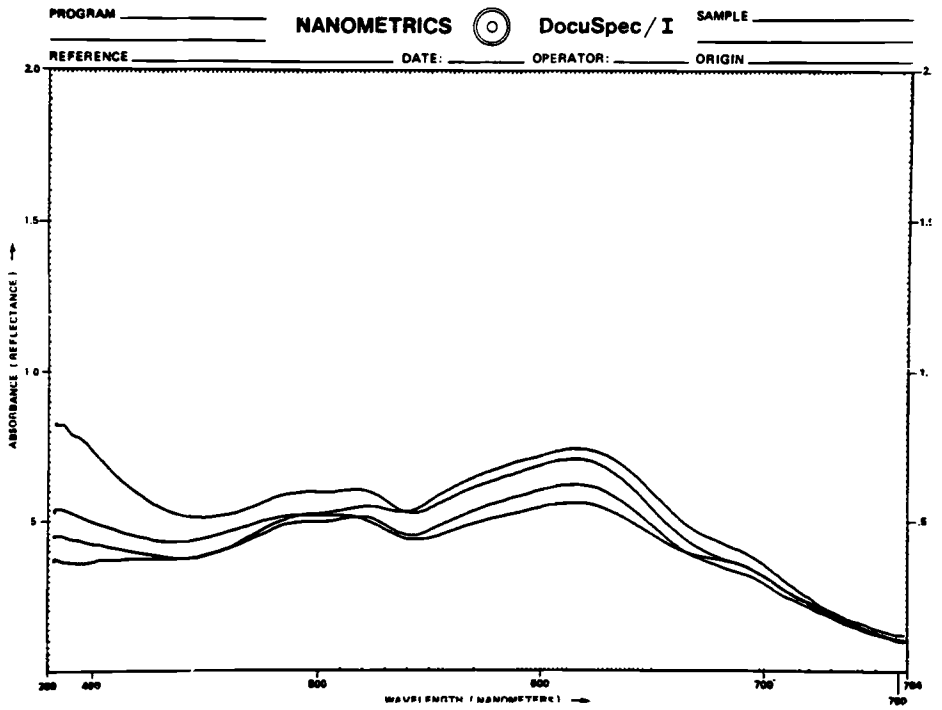

FIG. 4—*Transmission spectra of inked (black Parker roller ball pen ink) brown paper fibers in Permount.*

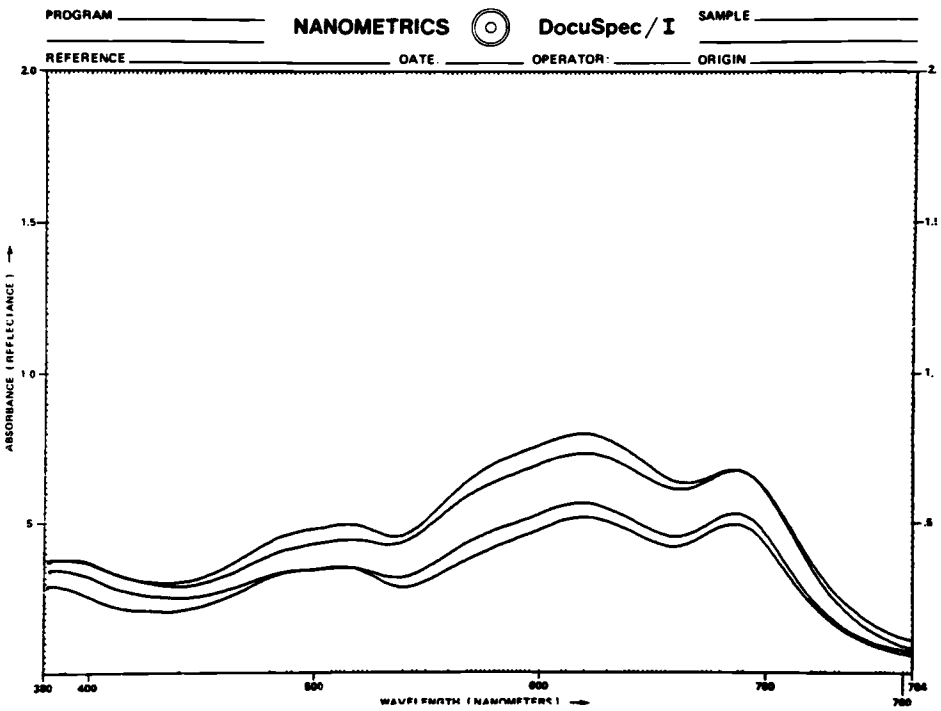

FIG. 5—*Transmission spectra of smeared inked brown paper fibers (the same ink as in Fig. 4).*

The spectra came from four different samplings of the inked brown paper. The maximum variability by the method of mounting was obtained with Parker floating ball blue pen on a brown paper: m.n. = 0.56 + 0.26 (Fig. 2); the variability for this ink by the smearing method was: m.n. = 0.09 + 0.07 (Fig. 3). The advantage of the former method is that smearing the inked fibers on glass slide increases the measuring area and decreases regions of high absorbance, thus improving statistics of measurement. Sometimes by the method of smearing it was possible to separate ink from fibers. In this way areas of ink without fibers' spectral interference could be obtained, which was especially important in the case of brown paper.

It was observed that in the case of some blue and black inks, the spectra of smeared inked fibers differ from spectra of respective unsmeared ink deposits on glass (Figs. 6 to 8). As can be seen, the differences may be quite large and not in the same manner. Usually the same phenomena occur when smearing respective ink deposits (not inked fibers). It was observed that changes in the spectra caused by smearing depend on the pressure applied during smearing (Fig. 9). Usually the maximum observed changes were achieved by exercizing moderate pressures. In any case, smearing was continued until no further changes (good reproducibility) in the spectra were observed. In some cases of ink deposits quite long drying periods are necessary to cause changes in their spectra by smearing. Thus, in the case of blue Parker floating ball ink deposit (Fig. 9), a period of several days drying was not sufficient to cause the change by smearing. It was necessary to dry it for about 24 h at 100°C to change the spectrum by smearing. On the other hand, in cases of inked fibers the changes by smearing may be affected almost immediately following writing, that is, without drying.

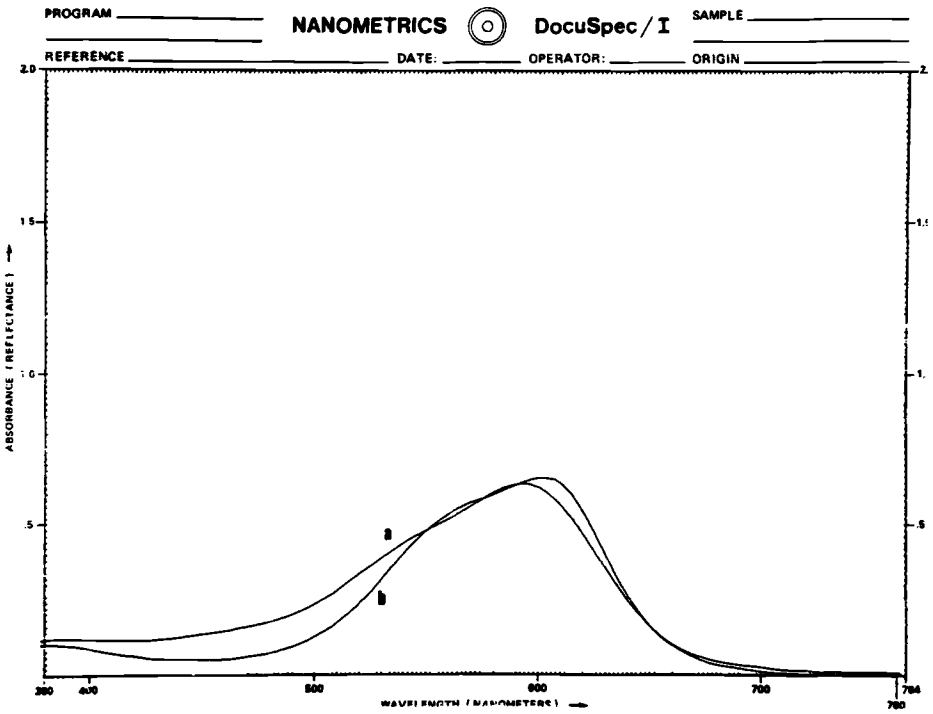

FIG. 6—*Transmission spectra of the blue Universal blue ballpoint pen ink:* (a) *is a spectrum of the ink deposit on a glass slide and* (b) *is a spectrum of smeared inked white paper fibers on glass.*

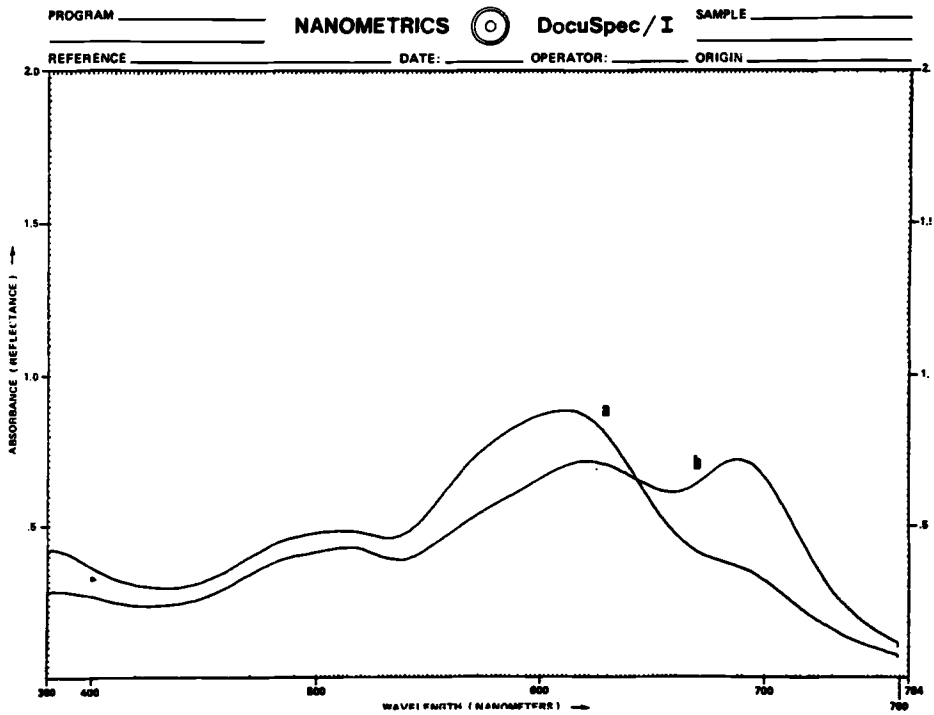

FIG. 7—*Transmission spectra of a black Parker roller ball pen ink:* (a) *and* (b) *as in Fig. 6.*

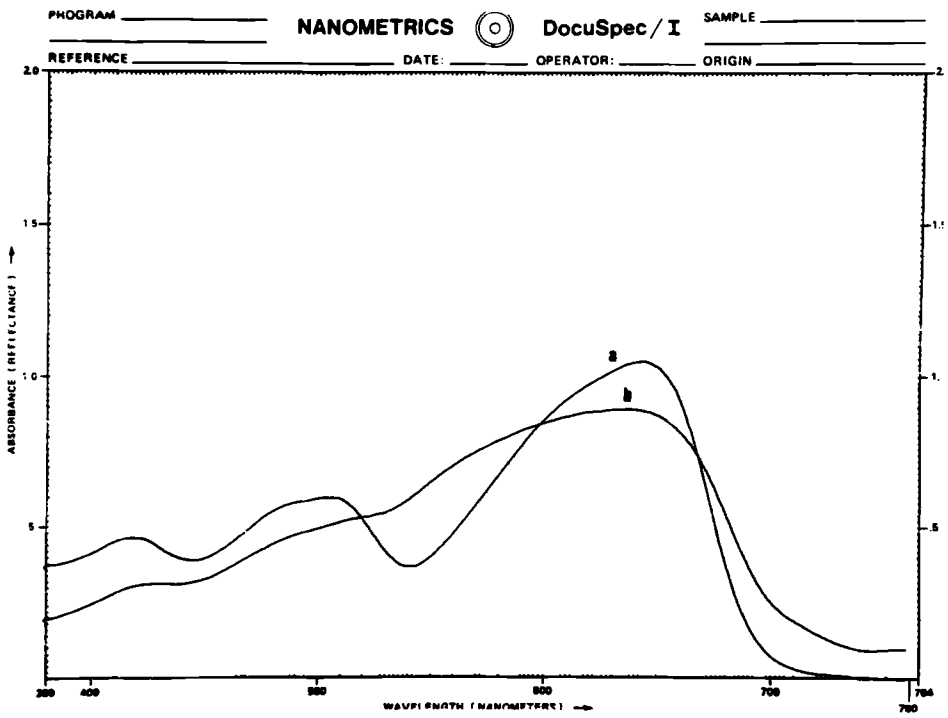

FIG. 8—*Transmission spectra of a black Mont Blanc quick pen fiber tip pen ink:* (a) *and* (b) *as in Fig. 6.*

Dissolving the smeared ink deposits on slides by solvents like methyl or ethyl cellosolve and drying usually restored the original spectra (before smearing).

In the case of a black stick ballpoint ink, some difference in spectrum was observed upon smearing the inked fibers (Fig. 10). However, we could not obtain a similar change by smearing the ink deposit on glass even after long heating periods at 100°C. In cases of other blue and black inks, a very slight change (if any) in their spectra occurs upon smearing their inked fibers or ink deposits (Fig. 11).

It should be pointed out that since pressures applied during smearing (crushing) of inked fibers by engraving tool on slides are much larger than may be exercised during writing, the variations in pressure during writing cannot influence the obtained spectra.

A similar phenomenon of a change in a spectrum upon smearing was observed in the deposits of copper phthalocyanine tetrasulfonic acid tetrasodium salt. As in the case of inks the change depended on applied pressure (Fig. 12). The change was reversed upon dissolving the smeared area in water and drying. A change in spectrum upon smearing had not been observed with the deposits of copper phthalocyanine pigment.

A much larger difference was observed in the X-ray diffraction spectrum between pressed and unpressed dyes in the case of copper phthalocyanine as opposed to the dye salt (with respect to results in visible spectrum). Therefore, at least for these species, there is no apparent correlation between changes in the crystallographic structure and changes in the visible spectra.

In the literature dealing with various derivatives of copper phthalocyanine [*8–11*] we have not come across the phenomena of a change in spectra due to applying pressure. The reports on variations in electronic spectra are due to a change in crystalline form

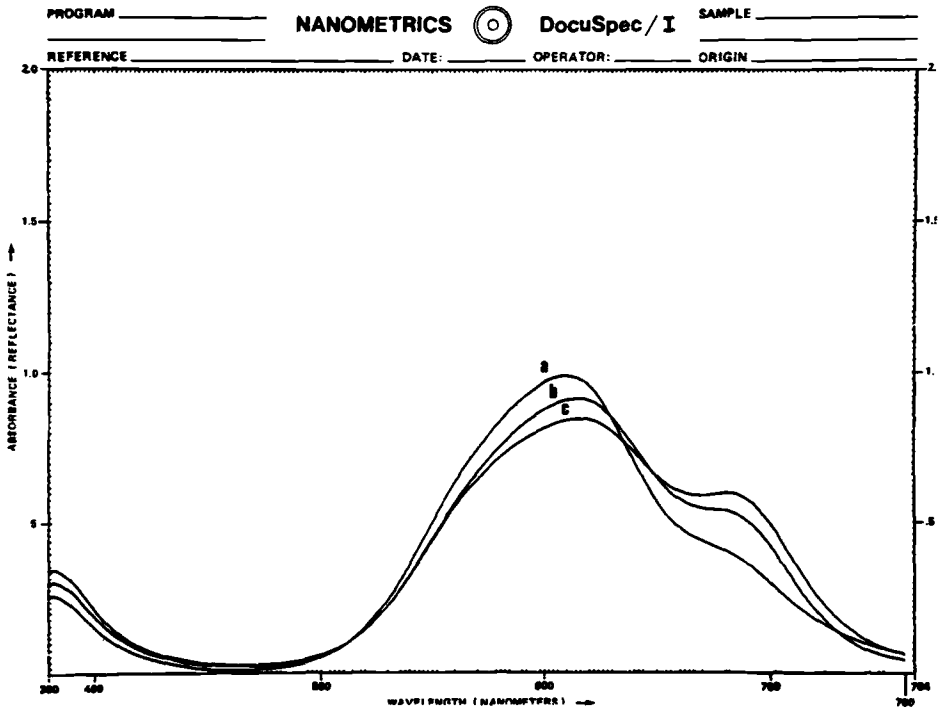

FIG. 9—*Transmission spectra of a blue Parker floating ballpoint pen ink:* (a) *is a spectrum of the ink deposit on a glass slide without smearing,* (b) *is a spectrum of the ink deposit smeared applying a small pressure,* (c) *is a spectrum of the ink deposit smeared applying a moderate pressure.*

($\alpha \rightarrow \beta$ transformation) in the case of copper phthalocyanine [*10*] or dimerization of phthalocyanine complexes in solution [*9*]. Changes in the electronic spectra as a result of aggregation were observed in dyes of many classes including cyanines, merocyanines, triphenylmethane dyes, xanthens, and so forth [*12–15*]. In many dyes, an absorption maximum was displaced to longer wavelength because of aggregation. The new band was called a *J*-band, and the aggregated state associated with the band could be referred to as the *J*-state. It may be possible that changes in the visible spectra of some inks and copper phthalocyanine tetrasulfonic tetrasodium salt upon pressure are due to changes in the relative concentration of species in various states of aggregation. In fact, in the case of copper phthalocyanine tetrasulfonic tetrasodium salt and some of the inks in the study (Figs. 7, 9, and 12) we can see that changes as a result of smearing while applying pressure are in a relative increase of the intensity of the peak at about 700 nm in comparison with the peak at about 600 nm.

Also, a different theory was proposed relating the apparent deviation from Beer-Lambert law to the degree of aggregation of four anionic azo dyes [*16*].

In any case, it seems that specific mechanisms explaining the changes of visible absorption spectra of various ink deposits caused by applied pressure may be the basis for additional extensive studies.

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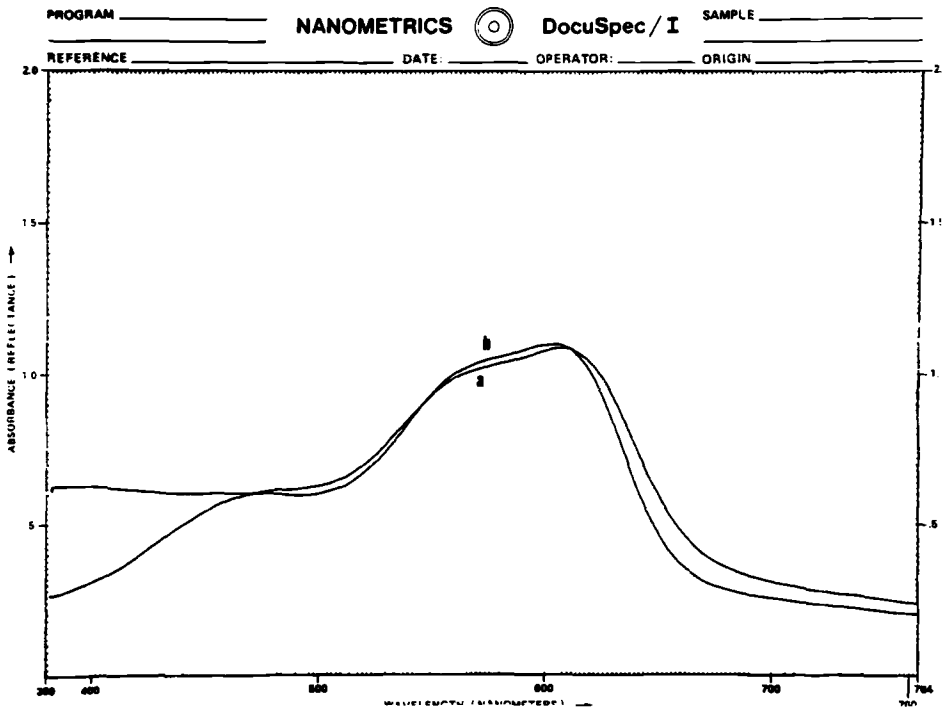

FIG. 10—*Transmission spectra of a black Stick ballpoint pen ink:* (a) *is a spectrum of the ink deposit on a glass slide and* (b) *is a spectrum of smeared inked white paper fibers.*

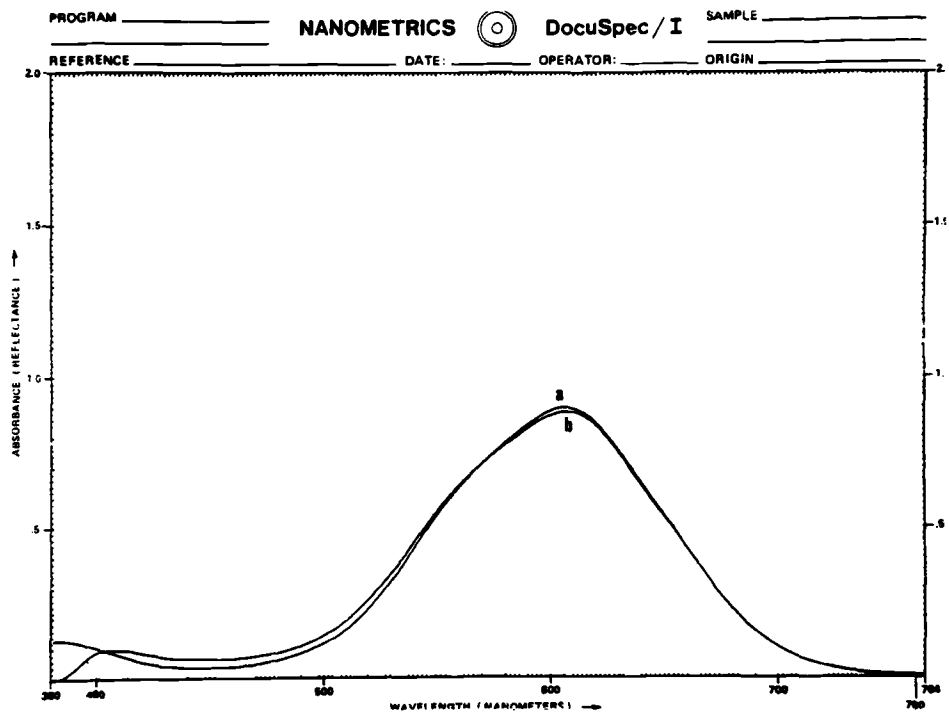

FIG. 11—*Transmission spectra of a blue Stick ballpoint ink:* (a) *and* (b) *as in Fig. 10.*

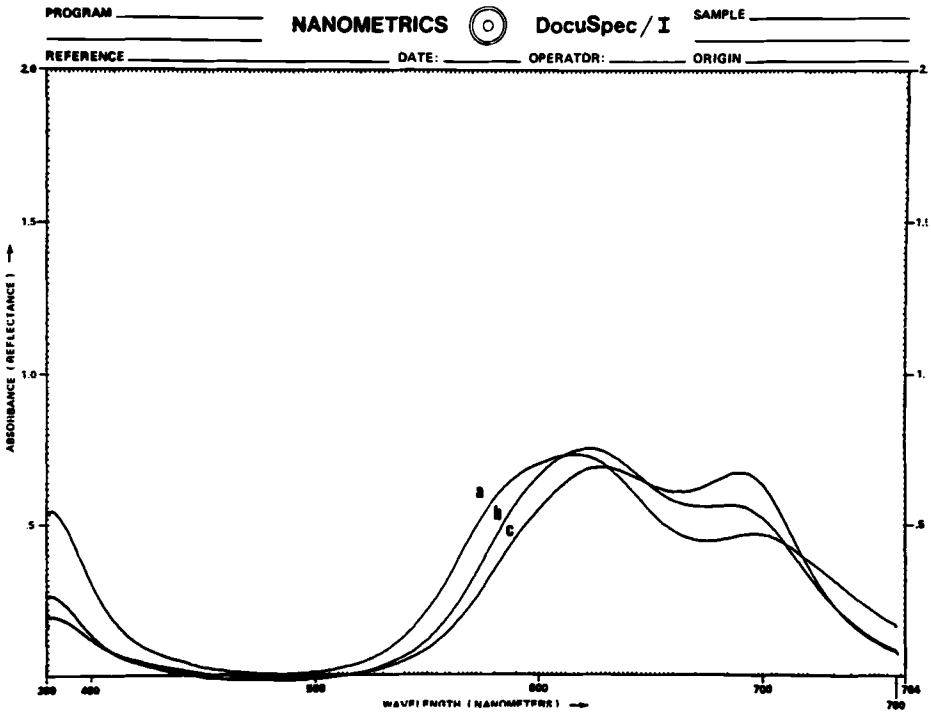

FIG. 12—*Transmission spectra of a copper phthalocyanine tetrasulfonic acid tetrasodium salt:* (a), (b), *and* (c) *as in Fig. 9.*

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