

A systematic approach to Egyptian ballpoint ink analysis for forensic science application

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ABSTRACT

The aim of this study was to establish the Egyptian standard ink library with its discrimination methods for differentiation among the locally produced ballpoint inks. Two groups of ballpoint inks were collected from various Egyptian sources, one of them contained four blue inks (inks 1-4) and the other contained four black inks(inks 5-8).

The results of ink identification obtained from non-destructive methods, such as filtered light examination (FLE) and microspectrophotometry (MSP) were compared with that obtained from Raman spectroscopy and Surface Enhanced Resonance Raman Scattering (SERRS).

The results show that only blue ink 1 was distinguished from the other blue inks 2, 3, and 4 by all physical tests, while the latter three inks could not be distinguished from each other by any one of the selected physical methods. Black inks 6 and 7 were distinguished from black inks 5 and 8 by all methods except infrared luminescence (IRL). Inks 5 and 8 were differentiated by SERRS.

Similar inks which could not be differentiated by the previous methods have been distinguished using thin layer chromatography (TLC). The results indicated that blue inks 2 and 3 are nearly the same inks .Blue inks 1 and 4 could be differentiated from each other and from blue inks 2 and 3. TLC could not distinguish black inks 6 and 7 and the results of energy dispersive X-ray analysis showed that they contained the same inorganic elements. They could be distinguished from inks 5 and 8. The later could be differentiated from each other by TLC and energy dispersive X-ray analysis.

It was concluded that SERRS is a complementary and very useful non-destructive technique to the common non-destructive technique. Energy dispersive X-ray analysis was found to be a rapid and sensitive technique that successfully differentiated the selected inks. Although TLC is a well established technique for the comparison of inks, it can be successfully replaced by the X-ray analysis.

Keywords:Forensic science, ink analysis, reflected infrared radiation, infrared luminescence, microspectrophotometry, Raman spectroscopy and surface enhanced resonance Raman scattering (SERRS), thin layer chromatography, scanning electron microscopy/energy dispersive X-ray analysis.

1. Introduction

Examination of suspect documents is one of the oldest branches of forensic science. The introduction of new writing materials together with increased literacy led naturally to an increase in the activities of the writing forger. Such forgery usually takes place in documents such as cheques, passports, birth certificate..... etc.

Over the past 40 years, document examiners have strived on the scientific examination and identification

of writing inks. Government agencies at all levels and lawyers in the private sector are using the examination of inks as a mean of establishing the authenticity or fraudulent nature of questioned documents.

Up to 1950, the development of more advanced techniques for analysing inks was slow because of the need to destruct even of small portions of the questioned document. Document examiners traditionally would not consider any test that would destroy the original condition of the document.

Before 1950, inks on questioned documents were

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primarily observed and examined by photography, using filters to enhance different contrasts between different ink[1]. Also the documents were additionally examined by observing the colours of inks under various wavelengths of light ranging from ultraviolet to infrared. Occasionally, chemical tests were used to detect metals such as copper, vanadium and chromium in fountain pen inks.

Although these methods have been accepted in courts for ink differentiation as they are not destructive to the document, they did not provide individual information to characterize the various formulations. In addition extreme caution should be exercised in accepting these methods as every test of them has its disadvantage or limitation.

Infrared luminescence (IRL) with dichroic filters and ultraviolet photographic techniques were initially used as non-destructive techniques for ink comparison to the field of ink comparisons[2-6]. On using IRL some tests are required to determine if the suspect ink contains both luminescent and masking components[4]. Ink profile uniqueness was improved by increasing points of identification using microspectrophotometry [7-10]. Forensic applications of this technique are restricted to cases where comparisons between samples are required.

During the past years courts have accepted the practice of removing very small samples from the questioned document for analysis[7]. In the early 1950s, Somerford and Sounder [11] used paper chromatography for the comparison of fluid inks. Their work showed that only a micro quantity of ink was necessary for the examination and the destruction to the questioned document was minimal and insignificant.

In 1966, Tholl [12] applied thin layer chromatography to ink analysis and reported that TLC could be effectively used for the separation of dyes as well as other non-volatile components of inks. His results were confirmed later by other researches [13, 14].

Over years numerous authors have discussed the value of other individual techniques including high-performance liquid chromatography [15], Capillary electrophoresis[16], laser-induced infra-red luminescence [17]

and Fourier transform infrared spectroscopy [18]and they have proposed standard protocols for forensic ink examination. However, there is little or no information regarding the application of a sequence of selected standard techniques (both non-destructive and destructive) to the Egyptian population of blue and black ballpoint pen inks.

Recently, Raman Spectroscopy and Surface Enhanced Resonance Raman Scattering (SERRS) have been used for the analysis of colorants. SERRS was found as a discriminative, sensitive and possible method to identify dyes in mixtures without prior separation [19]. Raman is much more like NIR, but no elaborate sample preparation is required. Also moisture attenuation is not a problem for Raman spectroscopy, which is a problematic in the IR. Nevertheless, the systematic research on the application of Raman in forensic science appears to be inadequate.

The aim of this study was to establish a complete systematic identification of Egyptian ballpoint pens. It was also interesting to see to what extent Raman spectroscopy and SERRS can be used to distinguish between various ballpoint inks in comparison with the traditional non-destructive physical methods, which were followed by TLC and energy dispersive X-ray analysis for further ballpoint ink discrimination.

2. Experimental

2.1 Sampling

The substrate used was uncoated paper supplied by Rakta paper manufacturing company, Alexandria, Egypt.

Four blue and four black ballpoint pens (the most commonly used pens), were collected from various Egyptian companies and coded with their data as shown in Tables 1 and 2.

Squares of approximately equal width and thickness were drawn using the tested pens (1 to 8) on paper sample. Each pen was used to write a pen code inside each square.

Table 1 Specifications of blue ballpoint inks

Code	Pen Name	Egyptian Company	Ink Manufacturer
1	Bic	Si-cep	under licence from Bic-France
2	Reynolds	Caico	under licence ; Reynolds-France
3	Kassco	Modern	A.K.F Germany
4	Rotamac	Pen-Tec	Documental Gmbh- Germany

Table 2 Specifications of black ballpoint inks.

code	Pen Name	Egyptian Company	Ink Manufacturer
5	Bic	Si-cep	under licence from Bic France
6	Reynolds	Caico	under licence ; Reynolds-France
7	Kassco	Modern	A.K.F Germany
8	Rotamac	Pen-Tec	Documental Gmbh-Germany

2.2 Procedures

2.2.1 Non-destructive Physical Experiments

Filtered Light Examination

Filtered light examination (FLE) was conducted using video spectral comparator (VSC 2000) , (Foster +Freeman company, England), with a tungsten halogen lamp. Various barrier filters between 400 -1000 nm were used. The instrument was used to analyze the following optical properties of the inks: reflected Infrared radiation with illumination in the near Infrared region (700-1000nm) and Infrared luminescence with excitation at 450 nm.

All the blue and black inks samples were simultaneously observed using VSC 2000. Each ink group were examined on one paper at the same time using the same wavelength, to avoid any change of light examination factors.

Microspectrophotometry

Microspectrophotometry test was conducted on the same samples used in the previous tests using a microspectrophotometer in VSC 2000 that uses visible/ infrared incident (2x20W halogen reflector lamps), with spectral range 400 to 1000 nm and 40 nm resolution.

Raman spectroscopy

The same samples used in FLE examination were analysed using the Foram 685 Raman Spectral Comparator (Foster + Freeman Company, England). For each ink, three spots were analysed and the mean of their spectra was then recorded and used for comparison purposes.

Surface Enhanced Resonance Raman Scattering

Fluorescence produced by many samples as a result of excitation with laser light in the visible region (685nm)

can be a major problem because it is more efficient than Raman signal. This results in swamping the Raman scattering. The whole analysis was then repeated after treating samples with a citrate reduced silver colloid solution [19]and poly (L-lysine) as an aggregating and quenching agent before analysis. Then the SERRS results were compared.

2.2.2 Semi-destructive Chemical Experiments

Thin Layer Chromatography

Two different TLC plates having different resolution and sensitivity were chosen: Macherey-Nagel precoated polyester TLC sheets, silica gel without indicator, "polygram sil G" and Merck precoated glass plates "silica gel 60F₂₅₄".

Each ink was diluted by absolute ethanol. Each diluted ink was spotted on the TLC plates using a 5- μ L micropipette at approximately 1.5 cm from one end of the plate, each ink group was spotted on separate TLC plate, i.e. blue inks 1-4 on one plate and black inks 5-8 on the other one. Spots were 2 cm apart from each other and 3 mm in diameter.

The dye components were separated using two developing solvent systems as detailed in literatures [6, 7,20,21]: solvent system I of ethyl acetate/ absolute ethanol/ distilled water (70:35:30 v/v), and solvent system II of n-Butanol /absolute ethanol / water (50:10:15 v/v).

Two sample sets were formed from each ink group, the first set was placed in a developing tank with solvent system I and the second set was placed in another tank with solvent system II. The tanks were closed tightly for 30 min.

The chromatograms were removed from the developing tanks and allowed to dry, and then they were examined under normal incident daylight, UV and near Infrared light.

The retardation factor, R_f , (the ratio of distance traveled by the compound to the distance traveled by the solvent) and colour tones of the separated bands

under various conditions were recorded.

Characteristic X-ray Spectroscopy

Energy dispersive X-ray analysis was used to quantitatively analyse the elements present in each ballpoint ink sample. For each ink, a thin layer was spread over a polyester sheet and left out to dry.

The specimen was placed on a carbon specimen mount with double sided tape and coated with gold in a vacuum for 20 sec.

Specimens were analysed using JEOL-JSM 5410 Scanning Microscope, Japan. The X-ray analyzer has SiLi detector using ISIS software(England). Three spots were analysed for each ink and the batch result (mean of the three readings) was recorded and used for comparison purposes.

3. RESULTS AND DISCUSSION

3.1 Filtered Light Examination (FLE)

Figs 1 and 2, respectively, show reflected infrared photographs of blue inks 1-4 and black inks 5-8 illustrating the visual results.

Each ink was photographed twice; The left photograph taken at the optimum excitation wavelength of 735nm for all blue and black inks and the right photograph at the optimum emission wavelength of 780nm for all blue inks, 850nm for black inks 5 and 8, 1000nm for black inks 6 and 7.

It is shown that the blue inks 2,3 and 4 were not distinguished from each other, but they were differentiated from ink 1.

Amongst the four black inks, inks 5 and 8 could not be differentiated from each other, but they were distinguished from inks 6 and 7.

Figs 3 and 4 show infrared luminescence photographs for blue and black inks, respectively. It is shown that the blue inks 2,3 and 4 were not distinguishable, with apparent difference from ink 1 (The same result as reflected infrared). This test failed to detect any differences between black ink samples.

3.2 Microspectrophotometry

Figs 5 and 6 show the microspectrophotometry spectral results for blue and black inks, respectively.

Considering blue inks spectra, Fig .5, spectral lines

for inks 2,3 and 4 are parallel to each other from the start to the end of the spectral range. Their maximum light absorption is in the region 550-600 nm and they transmit light completely at 780 nm. Ink 1 differs from them as it gives maximum absorption around 550 nm and complete transmission at 825 nm.

It is shown that blue inks 2,3 and 4 could not be distinguished from each other and are different from ink 1. These results confirm the results obtained from FLE results.

Considering black inks spectra, Fig. 6, it is obvious that spectral lines of inks 6 and 7 are parallel to each other from the start to the end of the spectral range. They gave maximum light absorption in the region 550-600nm. They did not completely emitted all the absorbed light until the end of the spectral range, 1000nm. Inks 5 and 8 gave maximum absorption in the region 500-600 nm and they are deviated from each other in the region 550- 850 nm then ink 5 emitted light completely at 925 nm, while ink 8 emitted it completely at 850nm.

It is shown that spectral results differentiated between inks 5 and 8 to some extent, but it failed in differentiating ink 6 from ink 7 which are already distinguished from inks 5 and 8.

3.3 Raman Spectroscopy

The results of Raman comparison of blue and black ink samples are shown as figures 7 and 8, respectively. Blue inks 2,3 and 4 could be distinguished from ink 1 (Fig. 7) since they showed straight lines due to the presence of fluorescent components which results in swamping of the Raman scattering[19]. Spectral results of black inks 6 and 7 are parallel and are differentiated from the spectral results of ink 5. Ink 8 gave a straight line.

3.4 SEERS

The results of SERRS comparison of blue and black ink samples are shown as Figs 9 and 10, respectively.

By considering blue inks' SERRS spectra (Fig. 9) the spectral lines of inks 2,3 and 4 are parallel to each other. These inks gave three distinctive peaks around 1200, 1425 and 1675 cm^{-1} in addition to weak peaks. Ink 1 gave four distinctive peaks around 750, 800, 1350 and 1600 cm^{-1} in addition to weak peaks.

SERRS results suggested that three of the blue inks namely 2,3 and 4 were of the same behaviour and could not be distinguished from each other.

By considering black inks SERRS spectra (Fig. 10), it is obvious that spectral lines of inks 6 and 7 are parallel to each other. These inks gave five peaks around 825, 950, 1200, 1400 and 1650 cm^{-1} . Ink 8 differed slightly from inks 6 and 7 as it contained a weak peak around 800 cm^{-1} ; and differed in the region 1300-1400 cm^{-1} . Ink 5 differed completely from inks 6, 7 and 8. It gave four peaks around 750, 800, 1350 and 1600 cm^{-1} .

SERRS results show that ink 5 differed from all other inks. Inks 6 and 7 were not distinguished from each other and they were slightly different from ink 8.

By comparing the results obtained by FLE with that obtained by Raman Spectroscopy and SERRS of different ink samples it led to:

Blue ink 1 could be distinguished from inks 2,3 and 4 by all tests, while these three inks could not be distinguished from each other.

Black inks 6 and 7 could not be distinguished from each other by any one of the previous tests. They could be distinguished from inks 5 and 8 by all tests except Infrared Luminescence. Filtered Light Examinations could not distinguish between inks 5 and 8. Microspectrophotometry could slightly differentiate between them. But they could be differentiated by Raman Spectroscopy and Surface Enhanced Resonance Raman Scattering.

3.5 TLC

Table 3 shows the colour bands and the R_f values of blue inks 1- 4 separated using Macherey-Nagel and Merck chromatograms, developed by solvent system I and II and observed under normal incident daylight.

From the results of Macherey-Nagel chromatogram with solvent system I, Ink 1 showed four separated bands and Ink 4 showed six separated bands. Inks 2 and 3 showed similar results as each of them showed six separated bands with the same R_f values.

On using Macherey-Nagel chromatogram with solvent system II, only ink 1 can be differentiated from the other blue inks.

Blue inks 2 and 3 showed the same bands and R_f values and could be differentiated from inks 1 and 4 using Merck chromatograms with solvent system II. Inks 1 and 4 behaved completely differently on using the same system. Merck chromatograms with solvent system I failed to completely differentiate the selected inks. Only ink 1 showed different chromatogram from inks 2, 3 and 4. The best results were obtained from Macherey-

Nagel chromatogram with solvent system I

Considering the colour bands and the R_f values of the black inks 5-8 using Macherey-Nagel and Merck chromatograms, developed by solvent system I and II under normal incident daylight, Table 4, it is obvious that:

In Macherey-Nagel chromatogram with solvent system I, Ink 5 showed four separated coloured bands. Ink 8 showed five different separated coloured bands and could be differentiated from ink 5. Inks 6 and 7 showed five similar separated coloured bands with the same R_f values. However they differ from the separated bands of inks 5 and 8.

Macherey-Nagel chromatogram with solvent system II, and Merck chromatograms with solvent systems I and II verified the above results.

The best results were obtained from Macherey-Nagel and Merck chromatograms with solvent system II.

The results obtained under UV and near IR lights confirmed the results obtained under normal incident daylight.

3.6 Energy dispersive X-ray analysis

Elemental composition of blue and black inks are shown as tables 5 and 6, respectively. It is shown that blue inks 2 and 3 contained the same inorganic elements. Ink 1 contained traces a small amount of Mg, while Cd was detected as a trace element minor component in ink 4. Also black inks 6 and 7 contained the same inorganic elements. Ink 5 and 8 had a high percentage of Cl but ink 5 had no Na.

4. Conclusion

Non-destructive physical methods such as reflected infrared, infrared luminescence and microspectrophotometry remain important valuable tools for the document examiners as they do not alter the visual morphology of the document. This is very important especially in the case of documents that have historical or financial value. Current findings indicated that examiners should use extreme caution in relying on these methods as every test of them has its disadvantage or limitation.

Surface Enhanced Resonance Raman Scattering (SERRS) technique can now be considered as a non-destructive method of ink analysis. It has advantages that make it favourable than the other non-destructive

techniques used for the analysis of colorants. There is no limitations and precautions before its application and it has a higher discrimination power. In our current work, SERRS successfully differentiated some of the selected inks (both blue and black inks). It distinguished inks 5 from 8 while the other non-destructive techniques failed to do that .

Similar inks, which could not be differentiated by the previous methods, were distinguished using TLC.

The results of TLC showed that blue inks 2 and 3 are of two similar compositions while blue inks 1 and 4 are different from each other and from inks 2 and 3. Black inks 6 and 7 are of two similar compositions while black inks 5 and 8 are different from each other and from inks 6 and 7.

TLC technique, therefore still has a very important role to play in the routine examination of inks , although a great deal of research is currently under way involving the evaluation of more sophisticated and sensitive instrumentation for ink analysis. Energy dispersive X-ray analysis successfully differentiated the selected inks (both the blue and black inks). It was found that, it is a rapid and sensitive technique, which makes it attractive for ink examination.

Our results and our final conclusion suggested that SERRS technique is a complementary and very useful non-destructive technique to the common non-destructive methods. Although TLC is a well-established technique for the comparison of inks, it can be successfully replaced by the energy dispersive X-ray analysis.

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Table 3 Thin layer chromatographic results of blue inks, solvent systems I and II , under normal incident daylight.

Chromatographic Medium	Solvent I				Solvent II			
	Ink 1	Ink 2	Ink 3	Ink 4	Ink 1	Ink 2	Ink 3	Ink 4
Macherey-Nagel	Blue 0.00	Pale blue* 0.11	Pale blue* 0.11	Purple 0.60	Blue 0.00	Pale blue 0.26	Pale blue 0.26	Pale blue 0.26
	Blue/purple 0.19	Pale blue* 0.27	Pale blue* 0.27	Purple 0.64	Blue/purple 0.33	Purple 0.63	Purple 0.63	Purple 0.63
Polyester TLC	Purple 0.57	Purple 0.60	Purple 0.60	Blue* 0.70	Purple 0.63	Blue* 0.70	Blue* 0.70	Blue* 0.70
Sheets silica gel Without indicator	Purple 0.72	Purple 0.64	Purple 0.64	Blue* 0.74		Purple 0.76	Purple 0.76	Purple 0.76
		Blue* 0.70	Blue* 0.70	Blue/purple* 0.80		Pale purple 0.83	Pale purple 0.83	Pale purple 0.83
Polygram SilG		Blue* 0.74	Blue* 0.74	Grey* 1.00				
Merck precoated	Blue 0.00	Blue* 0.00	Blue* 0.00	Blue* 0.00	Blue 0.00	Blue* 0.00	Blue* 0.00	Purple* 0.00
	Purple 0.32	Purple 0.29	Purple 0.29	Purple 0.29	Blue 0.30	Purple 0.39	Purple 0.39	Purple 0.39
Glass TLC	Purple 0.40	Purple 0.36	Purple 0.36	Purple 0.36	Pale purple 0.39	Blue* 0.45	Blue* 0.45	Blue* 0.45
Plates silica gel 60 F254	Blue/purple 0.58	Purple 0.45	Purple 0.45	Purple 0.45	Purple 0.45	Blue* 0.54	Blue* 0.54	Blue* 0.54
	Pale green 0.67	Purple 0.49	Purple 0.49	Purple 0.49	Pale purple 0.63	Purple 0.57	Purple 0.57	Purple 0.57
		Blue* 0.54	Blue* 0.54	Blue* 0.54	Pale blue 0.75	Pale purple 0.63	Pale purple 0.63	Purple 0.63
		Pale blue 0.60	Pale blue 0.60	Pale blue 0.60		Pale green* 1.00	Pale green* 1.00	Olive green* 1.00
		Pale violet 1.00	Pale violet 1.00	Blue* 1.00				

* Represents luminescent band.

Table 4 Thin layer chromatographic results of black inks, solvent systems I and II, under normal incident daylight.

Chromatographic Medium	Solvent I				Solvent II			
	Ink 5	Ink 6	Ink 7	Ink 8	Ink 5	Ink 6	Ink 7	Ink 8
Macherey-Nagel	Blue/ green 0.00	Purple 0.62	Purple 0.62	Pink (f)* 0.51	Blue/green 0.00	Purple 0.63	Purple 0.63	Pink (f)* 0.43
	Yellow 0.17	Purple 0.68	Purple 0.68	Purple 0.60	Pale yellow 0.17	Purple 0.73	Purple 0.73	Purple 0.56
Polyester TLC	Orange (f) 0.73	Purple 0.72	Purple 0.72	Yellow 0.66	Pale green 0.60	Yellow 0.86	Yellow 0.86	Purple 0.66
Sheets silica gel Without indicator	Blue 0.76	Grey 0.78	Grey 0.78	Purple 0.70	Orange (f) 0.73	Black 1.00	Black 1.00	Yellow 0.76
		Buff 0.98	Buff 0.98	Purple 0.74	Blue 0.83			
Polygram SilG				Blue 1.00				
Merck precoated	Blue/green 0.00	Purple 0.36	Purple 0.36	Purple 0.29	Blue/green 0.00	Purple 0.42	Purple 0.42	Purple 0.39
	Yellow 0.18	Purple 0.43	Purple 0.43	Purple 0.38	Green 0.30	Purple 0.61	Purple 0.61	Pink (f)* 0.45
Glass TLC	Yellow 0.32	Purple 0.47	Purple 0.47	Purple 0.47	Yellow 0.48	Purple 0.57	Purple 0.57	Purple 0.51
Plates silica gel 60 F254	Orange (f) 0.60	Pale purple 0.54	Pale purple 0.54	Pink (f)* 0.51	Orange (f) 0.60	Pale purple 0.63	Pale purple 0.63	Purple 0.57
	Blue 0.65	Grey 0.72	Grey 0.72	Purple 0.53	Blue 0.60	Black 1.00	Black 1.00	Pale purple 0.63
		Yellow/Brown 1.00	Yellow/Brown 1.00	Pale purple 0.58				Yellow 0.75
			Yellow 0.89	Pale purple 1.00				

(f) represents fluorescent band.

* represents luminescent band.

Table 5 Results of energy dispersive X-ray analysis of blue ballpoint inks.

Element % Ink Samples	Na	Mg	Si	Cl	K	Cu	Cd
1	18.98	4.02	9.02	29.47	4.67	33.84	--
2	20.17	--	43.60	12.39	0.53	23.30	--
3	17.31	--	38.36	14.74	2.83	26.76	--
4	22.57	--	21.93	30.08	--	18.65	6.77

Table 6 Results of energy dispersive X-ray analysis of black ballpoint inks.

Ink Samples	Element %			
	Na	Si	Cl	Cu
5	--	12.23	62.55	25.22
6	31.67	52.31	--	16.02
7	37.95	50.04	--	12.01
8	28.46	15.02	42.08	14.44

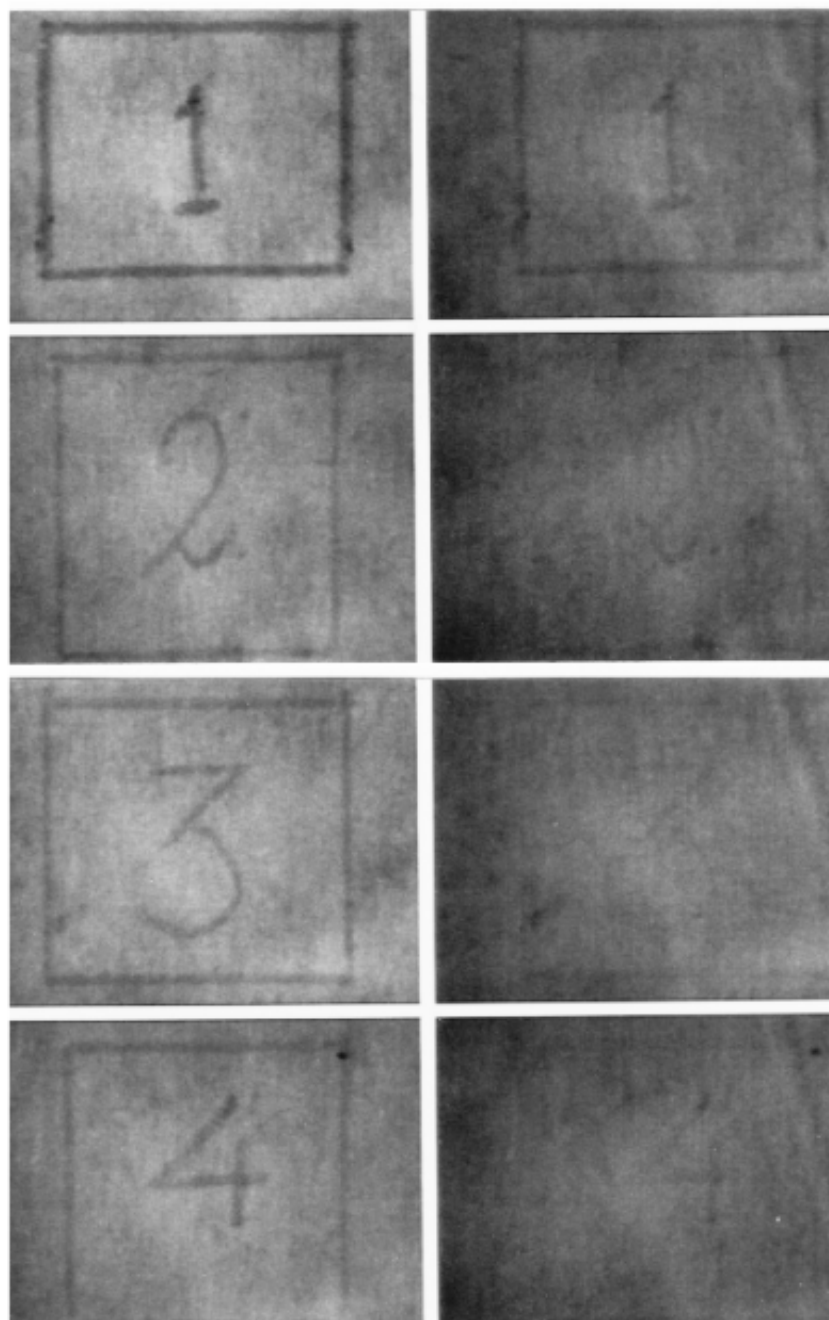


Fig.1 Reflected infrared photographs of blue inks (inks 1 to 4).

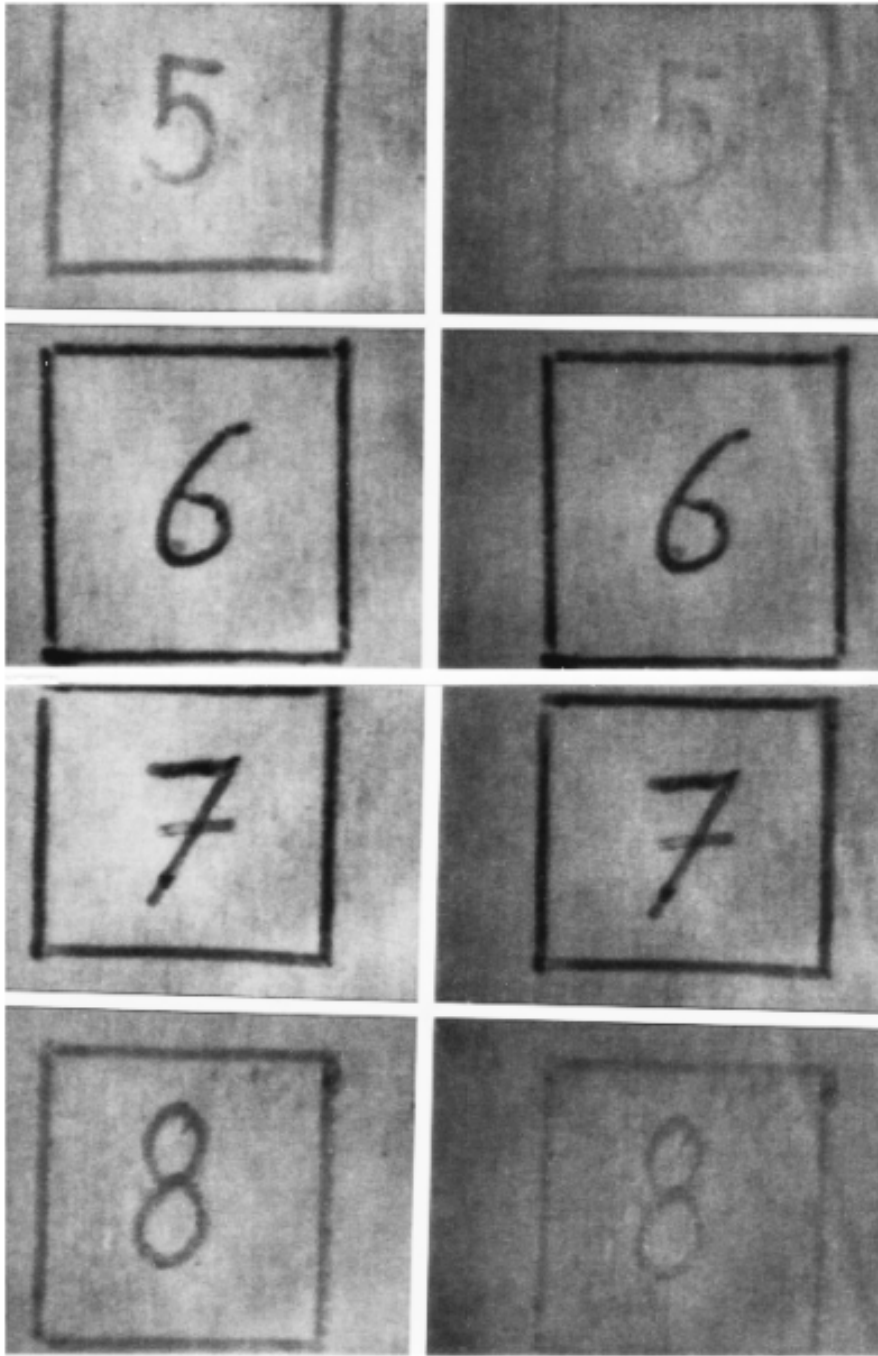


Fig.2 Reflected infrared photographs of black inks(inks 5 to 8).

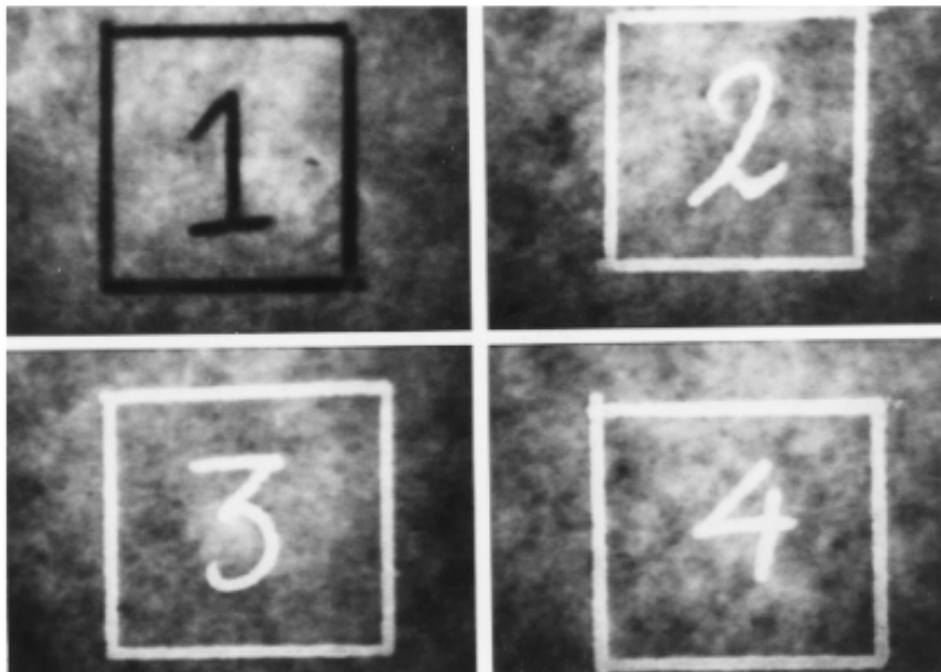


Fig.3 Infrared luminescence photographs of blue inks (inks 1 to 4).

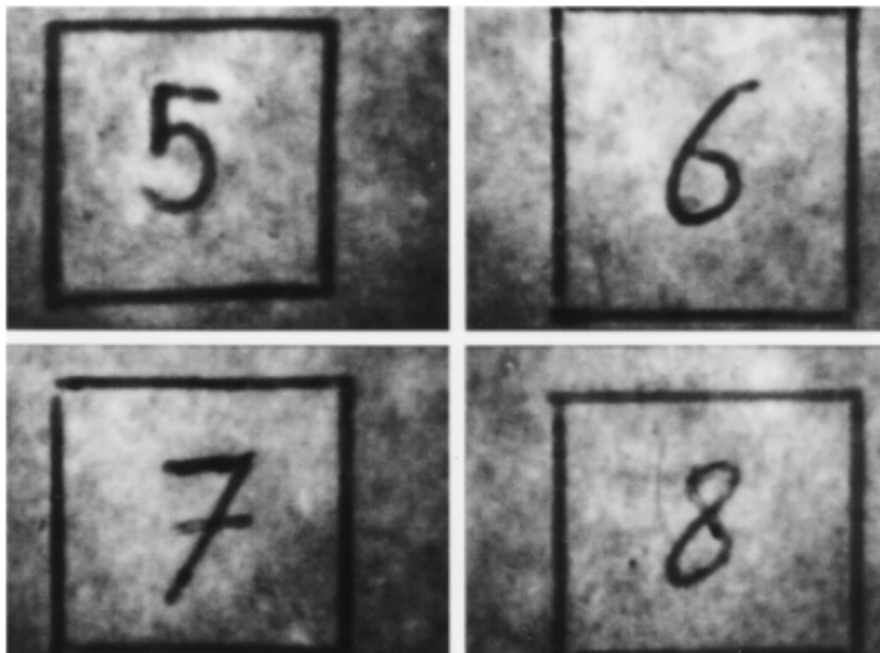


Fig.4 Infrared luminescence photographs of black inks (inks 5 to 8).

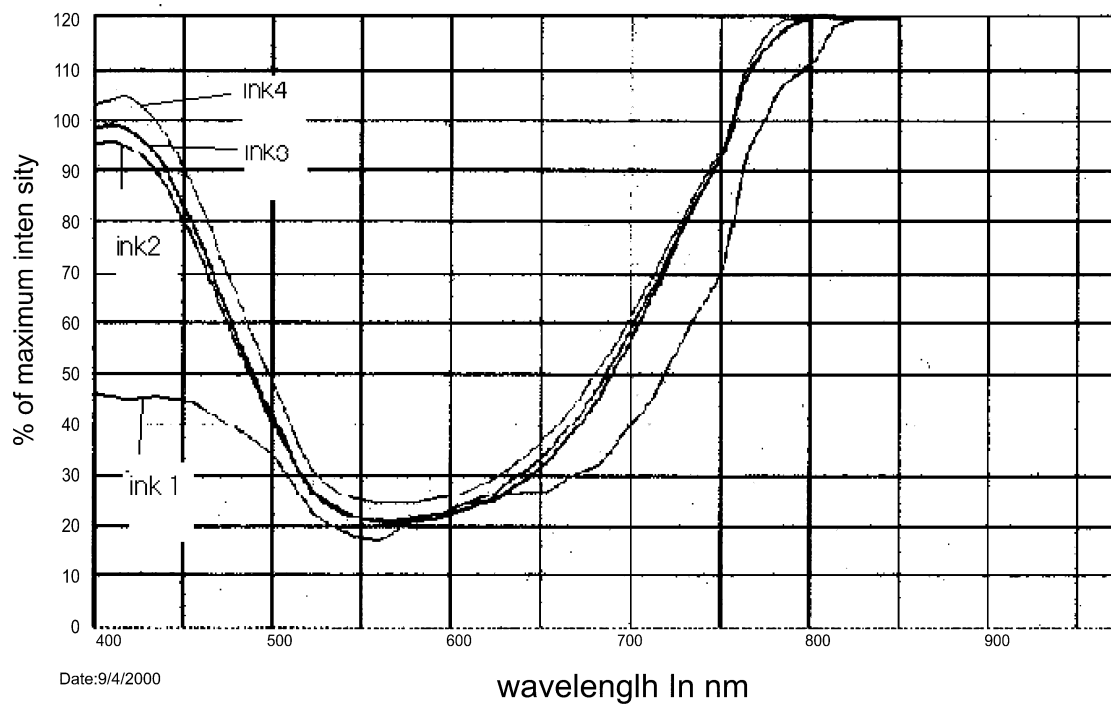


Fig.5 Microspectrophotometry spectral results of blue inks (inks 1 to 4).

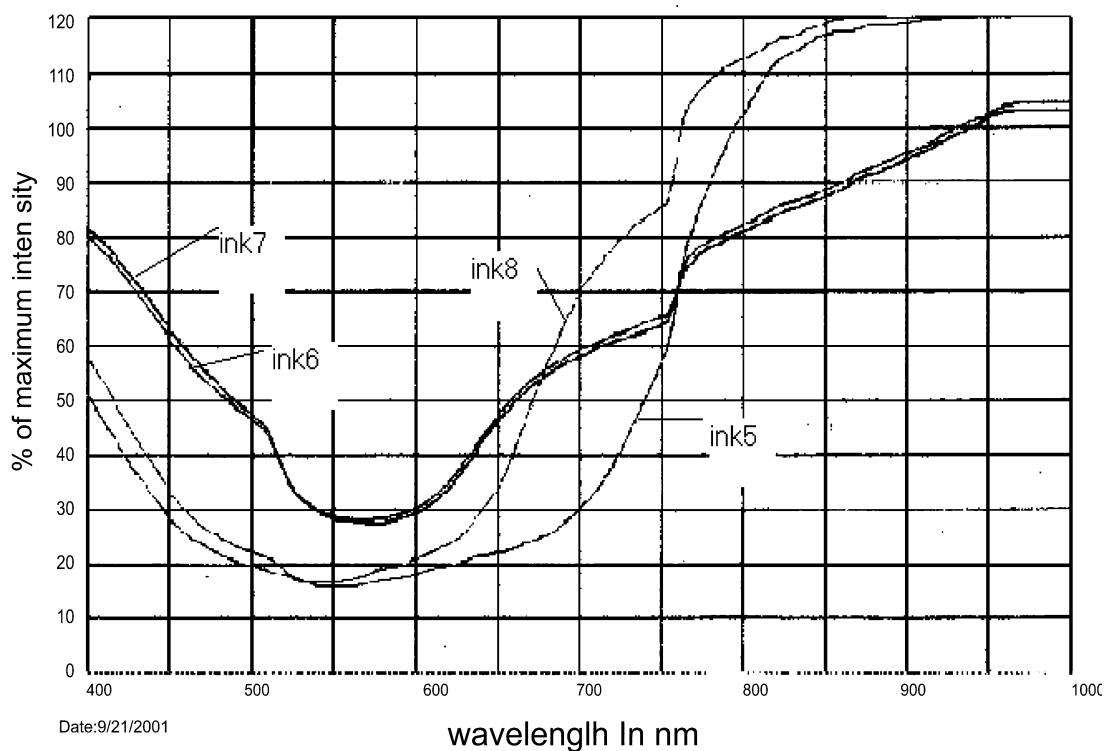


Fig.6 Microspectrophotometry spectral results of black inks (inks 5 to 8).

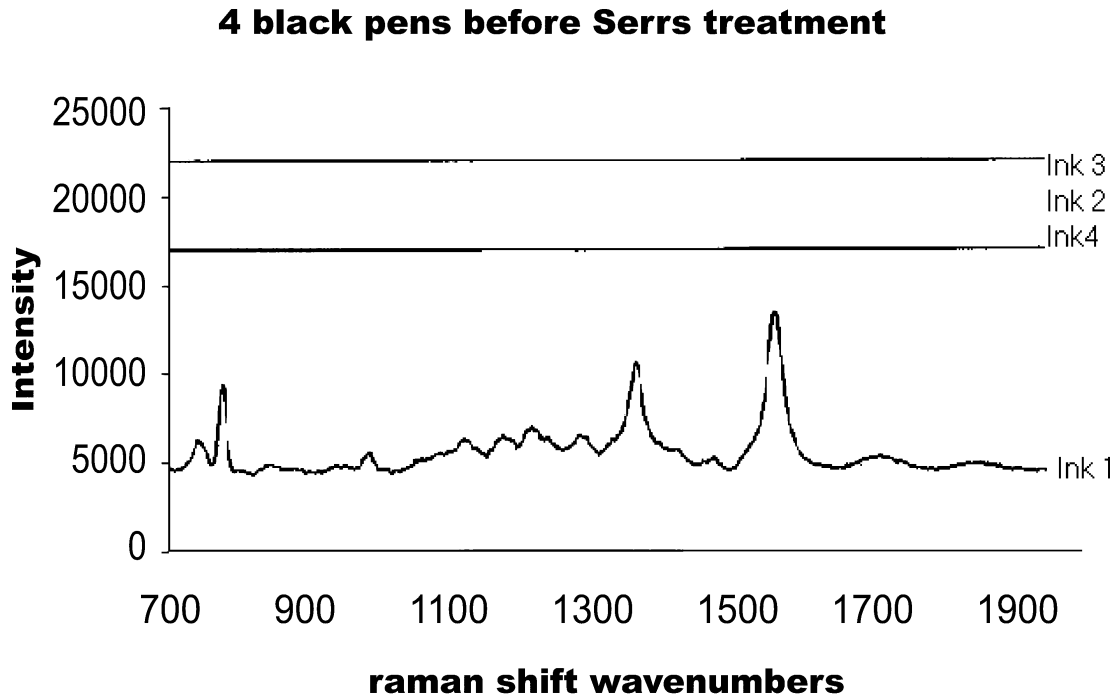


Fig.7 Raman spectral results of blue inks (inks 1 to 4).

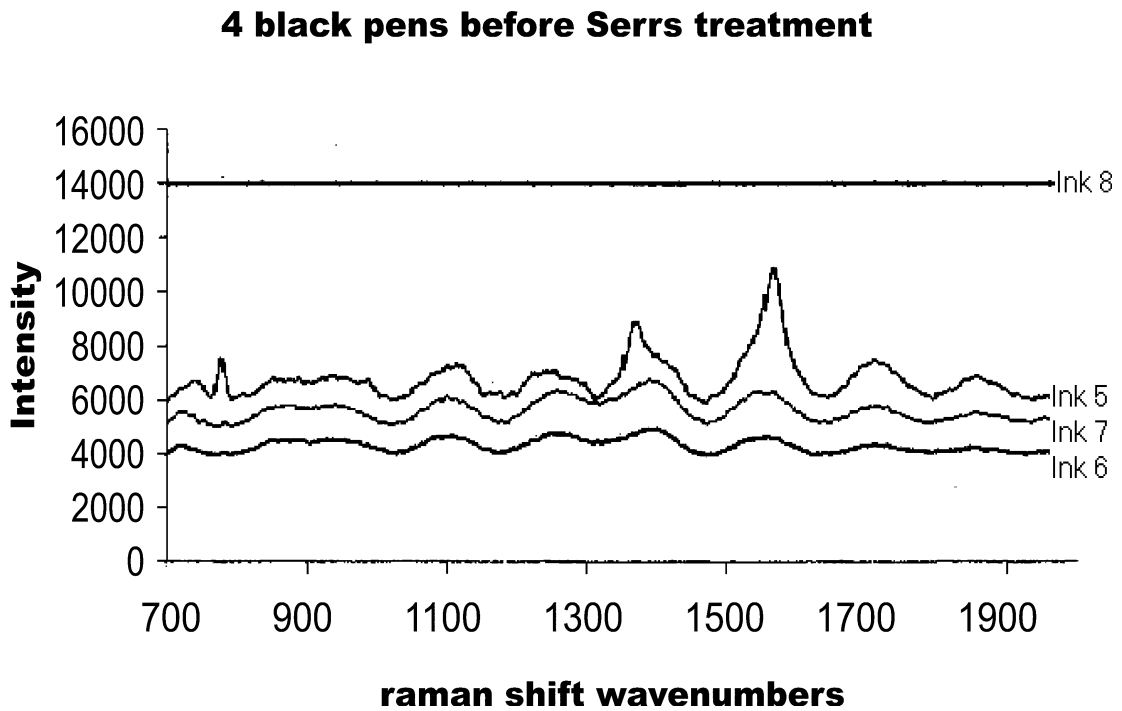


Fig.8 Raman spectral results of black inks (inks 5 to 8).

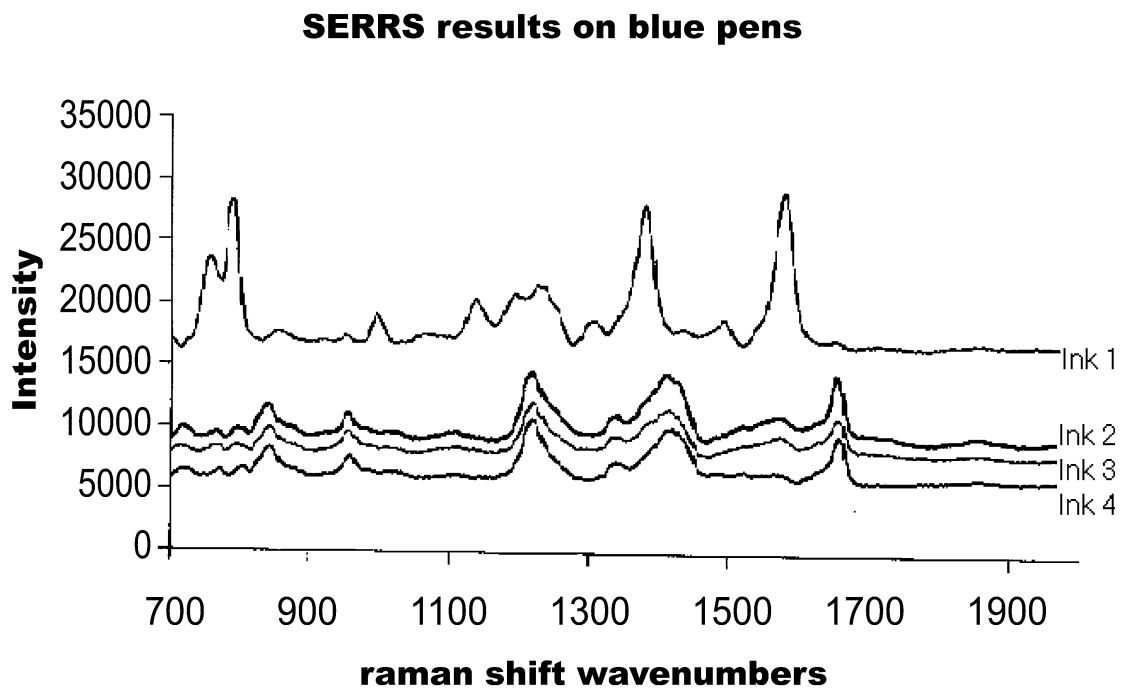


Fig.9 SERRS spectral results of blue inks (inks 1 to 4).

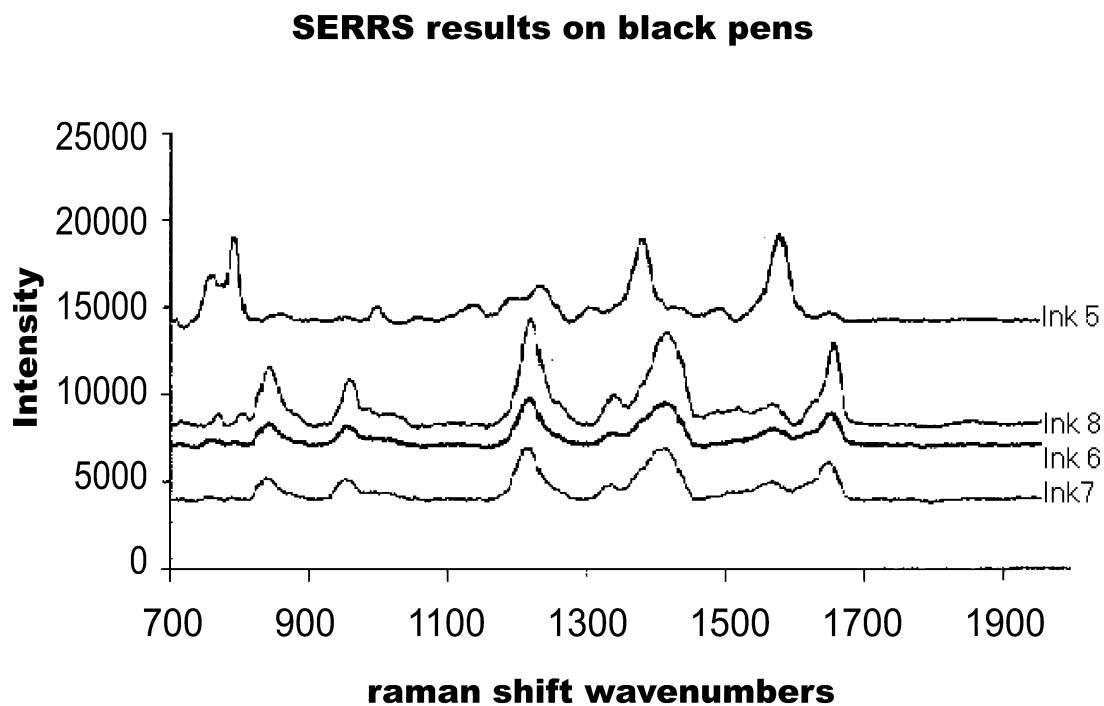


Fig.10 SERRS spectral results of black inks (inks 5 to 8).