DIFFERENTIATION OF BALLPOINT AND LIQUID INKS – A COMPARISON OF METHODS IN USE

Ewa FABIAŃSKA, Beata M. TRZCIŃSKA

Institute of Forensic Research, Cracow, Poland

ABSTRACT: The differentiation and identification of inks is a problem often encountered by experts in the examination of documents. There are two methods generally used to this aim: non-destructive – observation in visible light and infrared, and destructive method – thin layer chromatography (TLC). Infrared spectroscopy is also used, in conjunction with a microscope (MK-FTIR). This method is applied more rarely, as it gives worse results in the examination of ink samples taken from paper than in the analysis of pure ballpoint pen inks. It also demands a substantially larger amount of ink than TLC. Technological advances, in turn, have facilitated a rediscovery of Raman spectroscopy as a non-destructive method, used in the examination of writing lines among other things.

The aim of the tests conducted was to rate the usefulness of the four above-mentioned methods in cases of ink differentiation, which raise doubts.

The subject of the tests was black and blue ballpoint pen inks and liquid inks, that are in common use. Using optical methods and Raman spectroscopy, a line of writing applied to paper was analysed; for thin-layer chromatography, the ink was extracted from the paper while in the case of infrared spectroscopy , it was taken directly from the writing instrument.

The achieved results were analysed primarily assuming the possibility of distinguishing samples in VSC-1. In the case of inks which were indistinguishable or difficult to distinguish, the Raman spectrum was analysed, as were the chromatograms, and in the final phase, the infrared spectrum as well. It was found that the Raman spectroscopy method could serve as a supplement to the optical method. However, the destructive methods cannot be completely disregarded.

KEY WORDS: Ink; VSC-1; Raman spectroscopy; TLC; FTIR.

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INTRODUCTION

The dynamic technological advances in word processing and printing devices observed over the past decade has not fully eliminated handwriting. In addition to documents that are completely handwritten, many forms include positions which require filling out by hand. For this reason the identification and differentiation of inks remains still a problem for document experts. Because the chemical composition of inks and the construction of writing instruments are undergoing a constant modification, there is a permanent need to perfect analytical methods and procedures.

Spot tests, used until the 1950s for the identification of liquid ink have been completely discontinued, though thin-layer chromatography – being developed from paper chromatography – is still relatively often used. This technique, which primarily yields information concerning dyes, is indispensable as a screening method. However, when the examined materials contain identical dyes but differ in their content of other components, these can modify the resulting chromatograms and, consequentially, also be useful for ink differentiation. Other advantages to this technique include the relatively small amount of material needed for testing, is simplicity, and its low cost. The fact that there are databases that can be referred to in many criminalistic laboratories [2, 3, 9], which list the chromatograms of a wide variety of inks, is also relevant.

Because documents are a type of evidence that requires special treatment, researchers' efforts are aimed at seeking ever more sensitive techniques on the one hand, while developing ones that are non-destructive on the other. Capillary electrophoresis, which also derives from chromatography, is a method which shows particular promise. Despite the fact that this technique is destructive, it can be used to differentiate inks which are undistinguishable through thin layer chromatography [10], and requires a similar small amount of sample material.

However, due to its non-destructive nature, Raman spectroscopy is especially attractive to forensic experts. In the course of the last few years a technological revolution has taken place, which has greatly simplified the manufacture and use of such devices. The new generation of these spectrometers features an energy output of over 30% (the older types produced less than 1%); the time needed to take measurements has been shortened, and the laser intensity requirements have been lowered, which makes it possible to examine documents without destroying them (through burning). Another advantage to using low power lasers is their good signal-to-noise ratio. There is a new generation of compact, portable spectrometers devices now available. Thanks to all this, the method has proven useful to criminalistics in the detection and identification of explosives, narcotics, and the examination of micro-traces (fibres, paints, etc.), as well as the differentiation of inks.

For many years now, optical examination of inks under a broad region of electromagnetic radiation has also been widely used. Utilising the properties of absorption in infrared light and luminescence in visible and infrared light, which are characteristic for chemical components of writing materials, makes ink differentiation possible without the need to take samples from the document. In cases where substantial differences are detected, this method makes further analysis unnecessary, shortening the time needed for examination of a document as well as keeping it from getting destroyed [5, 6, 8].

The least common method used by experts in these types of examinations is infrared spectrometry, as it requires a substantially larger amount of sample material than thin layer chromatography and capillary electrophoresis do, and is more useful in the differentiation of ballpoint pen inks than liquid inks [1, 4, 7].

The aim of the studies presented here was evaluation of the four above-mentioned methods: non-destructive – optical examination and Raman spectroscopy, and destructive – thin-layer chromatography and infrared spectroscopy. These studies were inspired by situations in which the interpretation of obtained results posed a problem, as well as an opportunity to become practically familiar with the possibilities offered by the Foster and Freeman Limited FORAM 685 spectrometer, which was designed for the purpose of forensic analysis.

EXPERIMENTAL

The subject of the studies were four groups of the most commonly used inks on the Polish market. These were blue and black liquid inks from hard tip and roller pens, and blue and black ballpoint pen inks. Twenty different blue and fifteen black ballpoint pen inks were examined, as well as nine types of blue and three black liquid inks. Lines and handwriting samples of these inks were applied to plain, white paper. Every possible combination of two inks (each possible pair) from within each group was created. All of the inks were analysed using four different methods.

Optical examinations

Optical examinations were done using the Video Spectral Comparator VSC-1, made by Foster and Freeman, Limited of Great Britain. The level of absorption in the red and infrared, from 610 to 1000 nm, and luminescence in visible and infrared light from 455 to 1000 nm were observed in the applied lines and handwriting samples.

Raman spectroscopy

Raman spectrum measurements were taken using the FORAM 685 spectrometer. In the same manner as in the case of the optical examination, lines applied to paper were analysed, and the point for spectrum measurement was selected while examining a magnified image of the line on a screen. The spectrum was collected and processed electronically using software written especially for use with this type of spectrometer.

Thin-layer chromatography

Centimetre-long segments were cut from the ink line, and the ink was extracted using a mixture of dimethyl formamide and chloroform in proportions of 9:1. The extract was then applied to non-fluorescent Merck 5721 Silica Gel 60 plates. The eluent solution was a mixture composed of ethyl acetate, isopropanol, distilled water, and acetic acid in proportions of 30:25:10:1. The chromatograms were developed in a Chromdes Horizontal DS-Chamber for TLC, licensed to the Medical Academy of Lublin, Poland. They were analysed in visible and ultraviolet light (254 and 366 nm).

Infrared spectrometry

Infrared spectra were obtained from ink which was taken directly from the writing instrument, not immediately after samples were taken, but after they had dried on a neutral surface (glass). The spectra were collected using an FTS 40A spectrometer coupled with a Bio-Rad/Digilab UMA 500 microscope, using a thin-film technique with KBr pellets, under standard conditions. Unlike chromatography, optical and spectrometric methods do not differentiate inks on the basis of the dyes they contain, but from information provided by all of their components, primarily those present in significant proportions (main components), and those which strongly interact in given region of electromagnetic radiation. Using these methods consequently yields additional information on the chemical composition of the inks being examined.

Differentiation of inks through their infrared spectra is achieved based on the peaks position and their relative intensity, while in Raman spectroscopy the course and shape of the background curve – which depicts the fluorescence intensity of the examined material – is also relevant.

DISCUSSION OF RESULTS

Results obtained for each pair, created with inks from one of four groups were analysed, addressing the question of whether or not the method used differentiates the elements of a given pair. The answers were classified in three categories: positive (+), inconclusive (?), negative (–). In order to systematise the obtained information, the results of the optical examination were used as a starting point, in keeping with standard document examination procedure. It was decided that a positive result, indicating differentiation of the inks in a given pair, is sufficient that such cases not require examination by other methods. In situations where the optical method does not yield a positive result, an alternative differentiation technique must be sought. In these cases the results obtained using the remaining methods were considered. The results of this analysis were presented separately for each group of inks.

Blue ballpoint pen inks

There are 190 possible combinations of two within a group of twenty ballpoint pen inks. From all of these combinations it was impossible to differentiate only six pairs using the optical method, while in ten cases there were inconclusive. It must be emphasised that this result might be not objective and may depend on the amount of ink in a given segment of a writing line. For this reason, sixteen pairs were regarded as impossible to differentiate and qualified for further examination.

TABLE I. POSSIBILITY OF DIFFERENTIATION THROUGH OPTICAL METHOD

Number of pair		
Overall	Possible to differentiate	Impossible to differentiate
190	174	16

TABLE II. POSSIBILITY OF DIFFERENTIATION USING OTHER METHODS

Ink	Method	
	RS	TLC	FTIR
4 and 7	–	–	–
5 and 6	+	?	–
12 and 16	+	+	+
17 and 18	+	+	+
17 and 19	+	–	+
1 and 12	+	+	+
3 and 17	–	+	–
3 and 18	+	+	+
3 and 19	+	+	+
4 and 16	?	+	+
7 and 12	+	+	+
7 and 16	?	+	+
8 and 14	–	?	–
10 and 15	–	+	+
6 and 13	+	?	+
18 and 19	+	+	+

Different methods or their combinations were successfully applied for the differentiation between elements of a pair. For example:

– it was impossible to differentiate inks 4 and 7 by any method. All results obtained are the same. This pair consists of inks made by BIC,
– all three methods were adequate (inks 1 and 12. These inks come also from the same manufacturer, but in this case it was Pentel,
– the elements of pair 4 and 16 can be conclusively differentiated using destructive techniques.

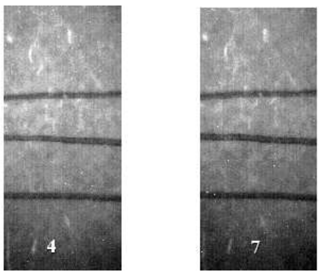

Fig. 1. Optical examination of inks 4 and 7 (λ = 645 nm, t = 0.6 s).

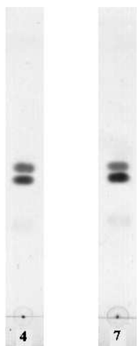

Fig. 2. Chromatograms of inks 4 and 7.

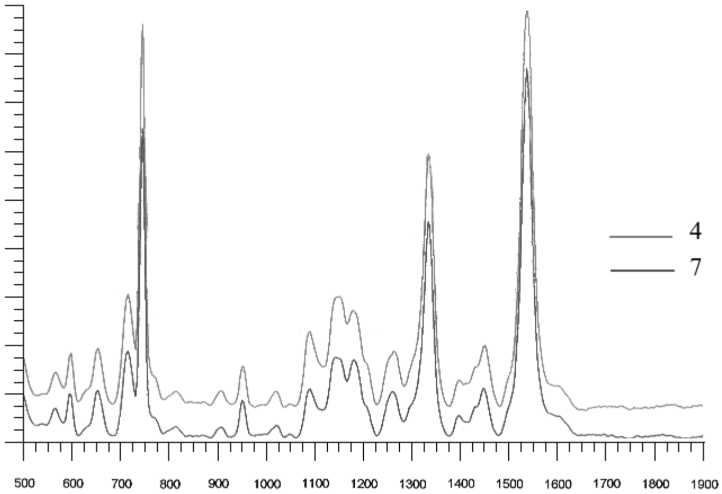

Fig. 3. Raman spectra of inks 4 and 7.

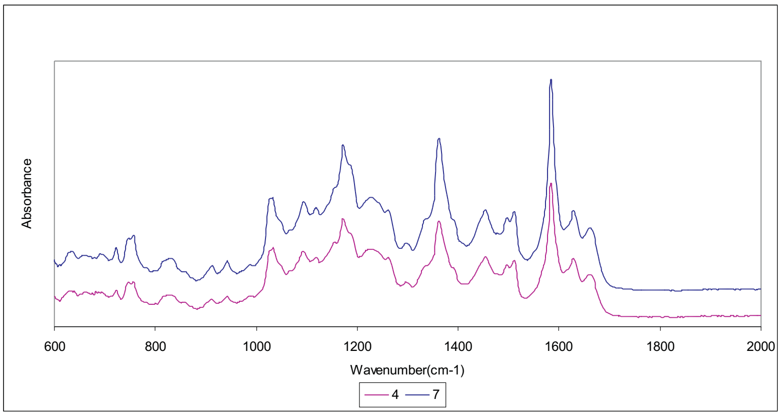

Fig. 4. Infrared spectra of inks 4 and 7.

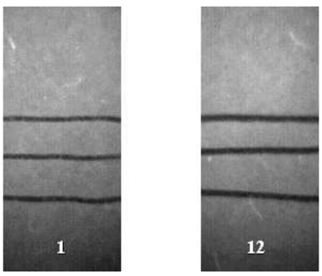

Fig. 5. Optical examination of inks 1 and 12 (λ = 630 nm, t = 0.3 s).

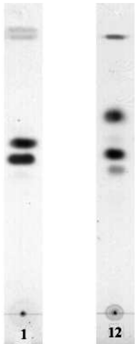

Fig. 6. Chromatograms of inks 1 and 12.

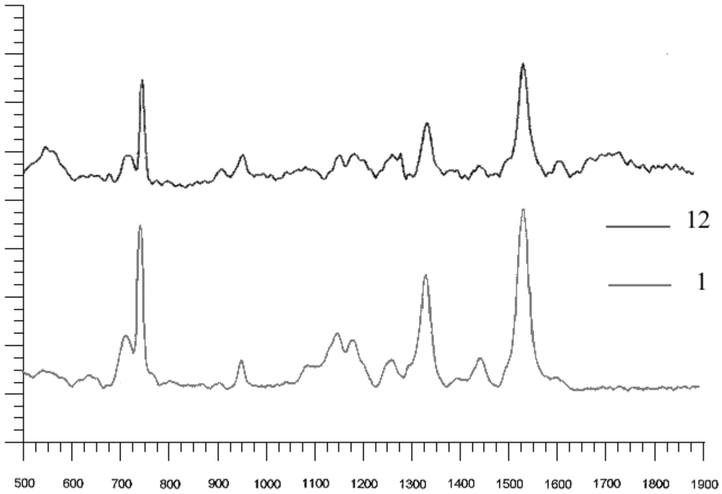

Fig. 7. Raman spectra of inks 1 and 12.

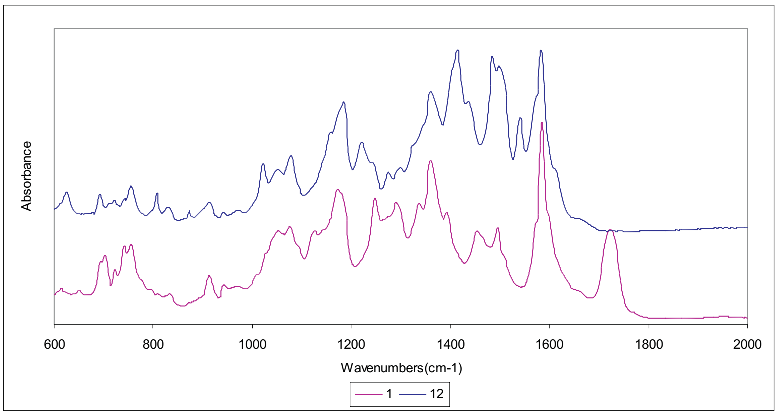

Fig 8. Infrared spectra of inks 1 and 12.

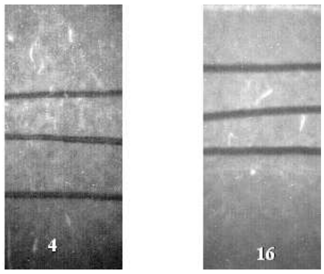

Fig. 9. Optical examination of inks 4 and 16 (λ = 645 nm, t = 0.6 s).

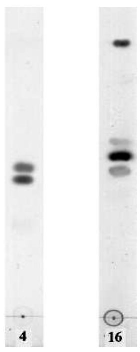

Fig. 10. Chromatograms of inks 4 and 16.

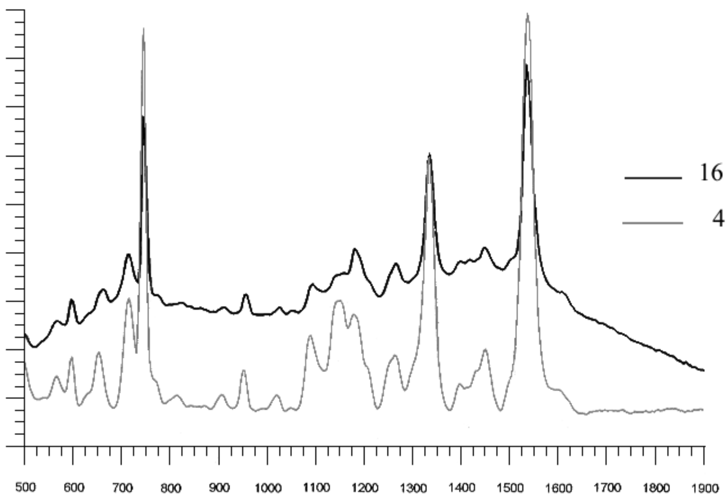

Fig. 11. Raman spectra of inks 4 and 16.

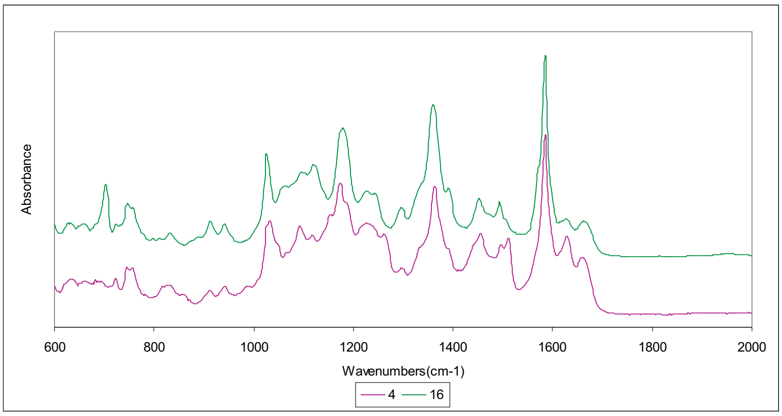

Fig. 12. Infrared spectra of inks 4 and 16.

Black ballpoint pen inks

The fifteen black ballpoint pen inks analysed created 105 different combinations of two. Among these, only three cases proved very difficult to differentiate using the optical method. After the remaining results had been included, it turned out that in the case of one pair of inks made by one manufacturer (BIC), differentiation was extremely difficult – just as in the case of that same company's blue ballpoint inks. It was possible to differentiate the other two pairs through at least one of the methods.

TABLE III. POSSIBILITY OF DIFFERENTIATION THROUGH OPTICAL METHOD

Number of pairs		
Overall	Possible to differentiate	Impossible to differentiate
105	102	3

TABLE IV. POSSIBILITY OF DIFFERENTIATION USING OTHER METHODS

Samples	Method		
	RS	TLC	FTIR
3 and 5	–	–	–
12 and 14	+	–	?
2 and 12	+	+	?

Results obtained for the BIC inks – pair 3 and 5, are identical. For pair 12 and 14, the key to differentiation lies in the Raman spectrum. The inks that make up pair 2 and 12 can be differentiated by three methods, though their FTIR spectra do not provide conclusive results.

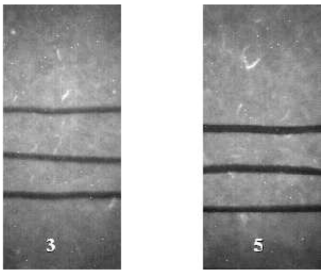

Fig. 13. Optical examination of inks 3 and 5 (λ = 665 nm, t = 1.2 s).

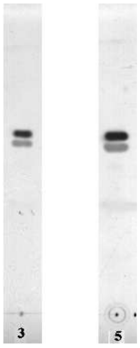

Fig. 14. Chromatograms of inks 3 and 5.

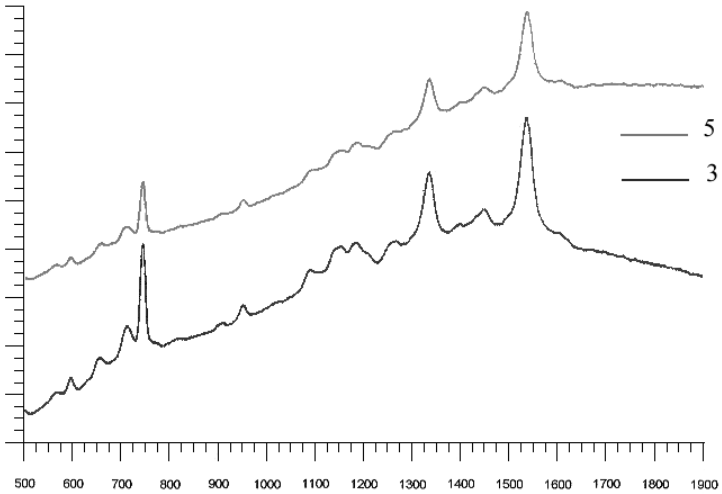

Fig. 15. Raman spectra of inks 3 and 5.

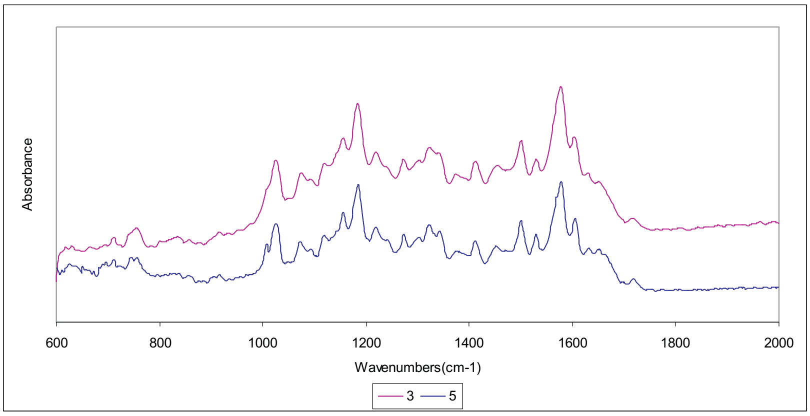

Fig. 16. Infrared spectra of inks 3 and 5.

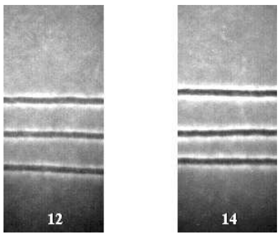

Fig. 17. Optical examination of inks 12 and 14 (λ = 630 nm, t = 0.6 s).

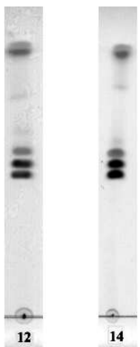

Fig. 18. Chromatograms of inks 12 and 14.

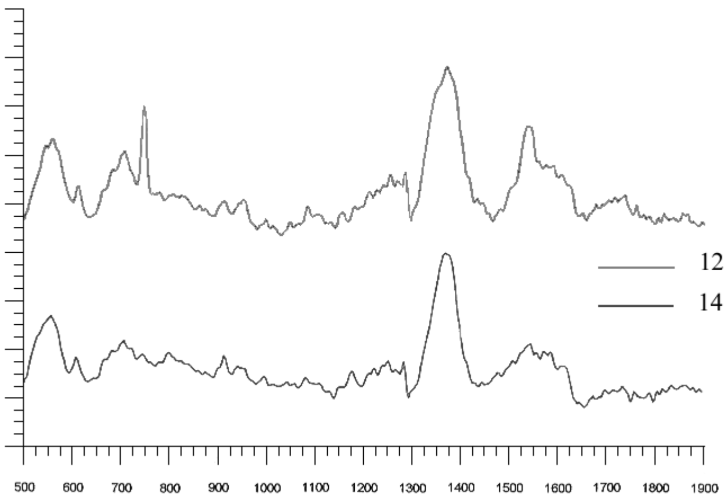

Fig. 19. Raman spectra of inks 12 and 14.

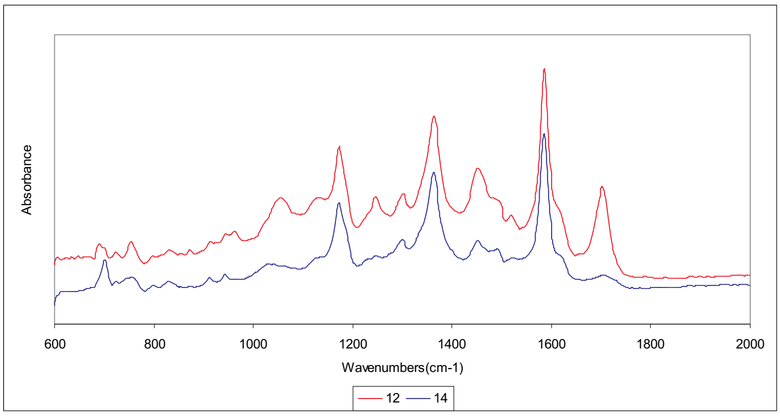

Fig. 20. Infrared spectra of inks 12 and 14.

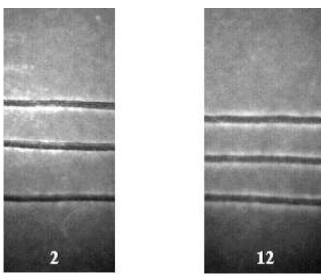

Fig. 21. Optical examination of inks 2 and 12 (λ = 630 nm, t = 0.6 s).

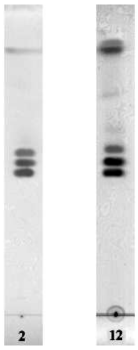

Fig. 22. Chromatograms of inks 2 and 12.

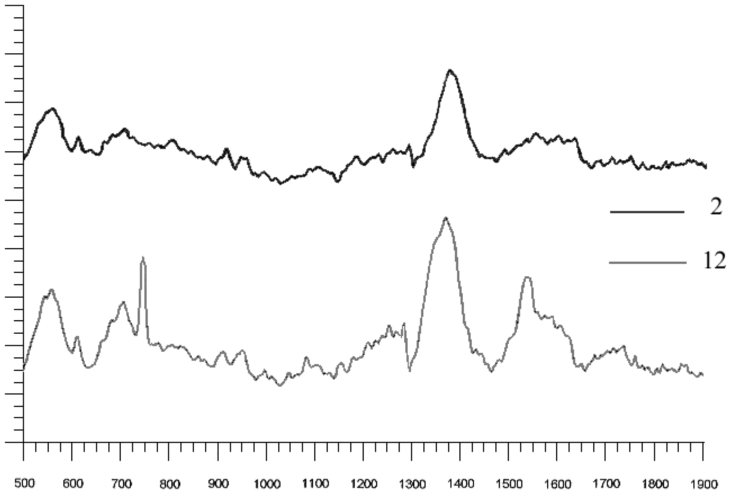

Fig. 23. Raman spectra of inks 2 and 12.

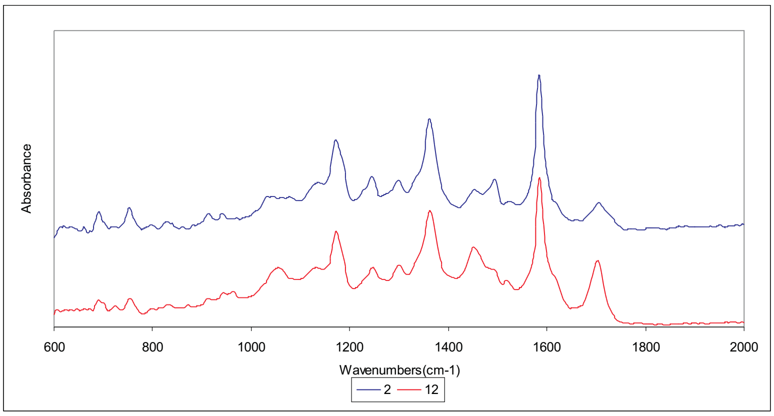

Fig. 24. Infrared spectra of inks 2 and 12.

Blue liquid inks

The group of blue liquid inks included nine samples, which made it possible to create 36 paired combinations. Of these, only two pairs were undistinguishable using the optical method. It also proved impossible to differentiate these inks using the other methods. In the case of one of the pairs, the results from every one of the methods were identical. For the other pair, the chromatograms and infrared spectra matched – however, due to overly strong fluorescence it was impossible to obtain the Raman spectra. It's obvious that in a situation where it is impossible to obtain not only a spectrum for both inks, but even a background line, their differentiation is impossible. However, when at least one of the inks has a measurable background, it is possible.

TABLE V. POSSIBILITY OF DIFFERENTIATION THROUGH OPTICAL METHOD

Number of pairs		
Overall	Possible to differentiate	Impossible to differentiate
36	34	2

TABLE VI. POSSIBILITY OF DIFFERENTIATION USING OTHER METHODS

Samples	Method		
	RS	TLC	FTIR
3 and 7	–	–	–
8 and 9	–	–	–

The discussed difficulties in differentiation are well illustrated by pair 3 and 7, where for both inks the results obtained are identical for every method used.

Fig. 25. Optical examination of inks 3 and 7 (λ = 630 nm, t = 0.6 s).

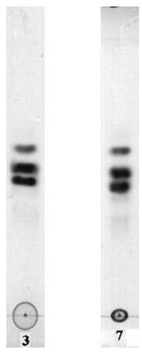

Fig. 26. Chromatograms of inks 3 and 7.

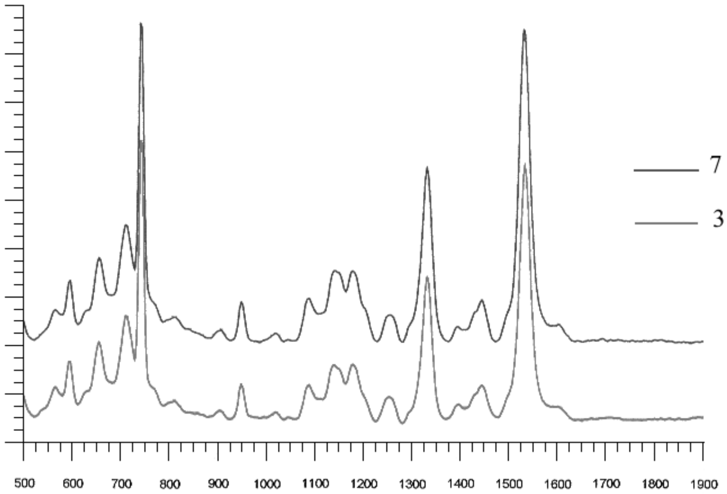

Fig. 27. Raman spectra of inks 3 and 7.

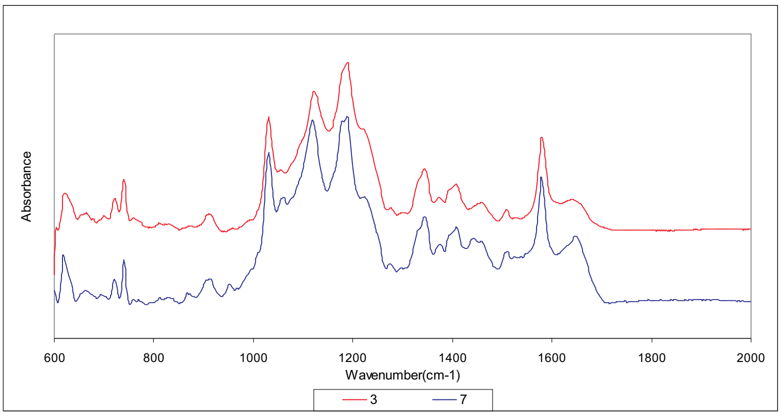

Fig. 28. Infrared spectra of inks 3 and 7.

Black liquid inks

The least numerous group of inks examined was that of three black liquid inks. They were distinguishable using the optical, as well as the other three methods. For this reason the results of those examinations will not be presented here.

CONCLUSIONS

Based on the obtained results, it can be said that optical examination as a tool for document expert can not be replaced by another method. Non-destructive Raman spectroscopy can be a valuable supplement to it. This is due to the fact that Raman spectroscopy provides different types of information about an analysed sample, thanks to which it can sometimes prove effective in cases that are difficult to determine on the basis of optical observations. Destructive methods, however, can not be completely resigned from, as there were pairs among the ones examined which could only be differentiated using thin layer chromatography.

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