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Application of micro-attenuated total reflectance FTIR spectroscopy in the forensic study of questioned documents involving red seal inks

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ABSTRACT

Red seal inks from Korea (6), Japan (1) and China (6) were studied to investigate the feasibility of micro-attenuated total reflectance (ATR) FTIR spectroscopy as a tool in the forensic study of questioned documents involving seal inks. The technique was able to differentiate red seal inks of similar colors and different manufacturers. Blind testing has shown that micro-ATR FTIR can identify the origin of the red seal inks with accuracy. Data gathered were converted to a database for future reference. Also, the technique was also successful in determining the sequence of heterogeneous line intersection from a personal seal and a ballpoint pen. The results show that micro-ATR FTIR can be a valuable non-destructive tool for the objective analysis of questioned documents involving different red seal inks.

1. Introduction

In East Asia, seal has traditionally been an impression of one's name that can be used instead of signatures in personal documents, office paperworks, contracts, art or any item requiring acknowledgement or authorship. China, Japan and Korea currently use seals and/or hand signatures [1]. Pen ink and seal ink analysis are therefore an important forensic procedure which can answer questions regarding disputed sensitive documents with significant financial values such as insurance claims, wills, contracts and tax returns [2,3]. The three most significant problems in involving inks are the following: characterization/differentiation of inks, sequencing of intersecting lines and dating of inks in documents [4]. However, ink analysis is usually done to know the origin of the ink or seal inks used or to determine the sequence of intersecting lines. An addition or alteration of a signature in a will or contract can dramatically change the terms of an agreement. However, if for example, the added signature intersects with a personal seal, then the alteration may be detected by examining the order of strokes [5].

There are two main types of line intersections, which are homogeneous and heterogeneous. A homogeneous line intersection is defined as one where line crossings have been produced using the same type of writing instrument while a heterogeneous line intersection is one where two different types of writing instrument have been used to produce line crossings (example: personal seal and ballpoint pen) [5].

The analysis of inks is divided into two categories: destructive and non-destructive. In destructive method, portion of the document with the ink has to be removed prior to analysis. Thin layer chromatography (TLC), high performance thin layer chromatography (HPTLC), high performance liquid chromatography (HPLC), and gas chromatography (GC) are some of the methods that fall in the first category [2,3,6,7]. On the other hand, non-destructive method involves the observation of ink on the documents by means of reflectance technique that allows the observation of the inks spectral characteristics without any alteration of the document [2]. In routine examinations of inks, non-destructive methods such as microscopy and optical ones, are applied first and, more often than not, this method is more desirable than destructive method since it keeps the evidence intact for further testing or review at a later date [3,7].

Whether analyzing inks to know its origin or examining documents for line intersection, the difficulty lies on the fact that most ink examination process remains manual and subjective, which are suffering from drawbacks from human interpretation [5,6].

Therefore, an ideal technique would be something that is non-destructive and can provide an objective method of analysis for a variety of materials that is possible to be encountered.

Raman spectroscopy was used in several forensic applications including the analysis of paints, fibers, explosives, illicit drugs, firearms discharge residues and in ink and document analysis [4,8,9]. Time-of-flight secondary ion mass spectrometry

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Table 1
Origin, brand names and colors of seal inks available commercially in Korea.

Sample no.	Origin	Brand names	Colors
S1	Korea	Mae Pyo (general)	Purple red
S2		Mae Pyo (general)	Red
S3		Mae Pyo (gold)	Purple red
S4		Mae Pyo (gold)	Red
S5		Peace	Purple red
S6		Peace (accent)	Red
S7	Japan	Compact	Red
S8	China	Ju-An	Red
S9		Guem-Ja	Red
S10		Kang-Sa	Red
S11		Toe-Ju	Red
S12		Kwang-Myung	Red
S13		Mi-Ryo	Red

(TOF-SIMS) was also reported to have been used in the non-destructive analysis of questioned documents. Inks were successfully discriminated and the sequencing of intersecting lines were resolved [3,10]. On the other hand, Fourier transform infrared (FTIR) imaging was already used in various forensic examinations [5–7]. Infrared imaging can be used to directly visualize the components of the sample, such as in the analysis of intersecting lines. Moreover, it gives the option of examining the specimen without pretreatment [5,7,11,12].

This study attempts to test the capability of micro-FTIR in an attenuated total reflectance (ATR) as a non-destructive tool to objectively determine the origin of the seal ink from its database and to determine the order of recording for heterogeneous intersecting lines involving a personal seal and a ballpoint ink.

2. Materials and methods

The stationery shops in Korea were exhaustively searched for red sealing inks. A total of thirteen red seal inks available commercially in Korea were purchased in local stationery shops. Their origins, brands and characteristic colors were noted (Table 1). Double A™, from Thailand was the white paper used throughout the study. Seal inks were individually stamped on the white paper leaving an imprinted personal seal. Ten minutes is allowed for the seal to dry after which their characteristic FTIR spectra were recorded and collected to make a seal ink database. Blind tests were done by stamping personal seals using the seal inks that are included in the seal ink FTIR database. These were labeled with codes to avoid bias.

For the study of the heterogeneous intersecting lines, black ballpoint pen from Barunson™ (Korea) was used. The spectra of this black ballpoint pen ink on paper were recorded. In this experiment, two scenarios were made, which are: (a) seal over black ballpoint pen ink and (b) black ballpoint pen ink over a seal. Each of these specimens was examined using micro-ATR FTIR and their spectra were subtracted with the IR spectrum of white paper.

2.1. Fourier transform infrared spectrometry

In this study, an FTIR spectrometer (Thermo Mattson, Infinity Gold FT-IR, Waltham, MA, USA) equipped with an IR microscope (SpectraTech, Inspect IR plus, Franklin Lakes, NJ, USA) with a mercury cadmium telluride detector was used to record the IR spectra of the samples. Sixty-four scans were collected with a resolution of 8 cm^{-1} and the frequency range was measured between 600 and 4000 cm^{-1} of the mid-IR region. Samples were mounted in the sample holder and no additional sample preparation was done. Spectrum of the white paper was recorded and this served as the blank throughout the experiment. Several spectra of the blank paper were done to check for the reproducibility. Since micro-ATR mode of the FTIR was used, spectra of the red seal ink and ballpoint ink were not swamped by the spectra contributed by the paper originating from the cellulose and other inorganic components which was also observed by Bojko et al [5]. Samples were measured in triplicates.

2.2. Spectral library and database

All IR spectra were gathered and used to build a spectral library using the Omnic™ software package [Thermo Nicolet Corp., Madison, WI, USA]. Properties of each spectrum, brand, country of origin and color/shade were included in the database. Queries can be run to match the unknown's spectrum with the data in the database.

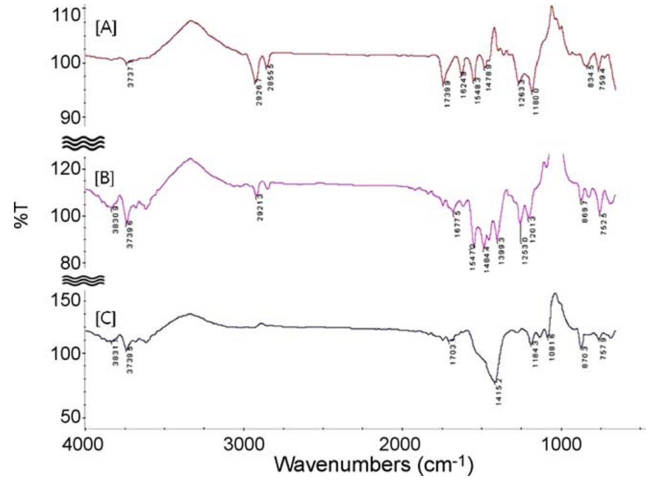

Fig. 1. Typical ATR FTIR spectra for seal inks of the same color but different manufacturer (A) a seal ink sample, S6 (B) a seal ink sample, S7 (C) a seal ink sample, S8. These IR spectra for seal inks stamped on white papers were subtracted with the IR spectrum of white paper.

3. Results and discussion

To differentiate the seal inks, each seals smeared with different seal inks were stamped on the standard white paper and FTIR recordings were done. FTIR data were collected and used to build a database. The number of peaks as well as the peak positions and relative intensities were analyzed and were used as the basis for differentiation. Results show that the micro-ATR FTIR can differentiate seal inks having the same color but different manufacturer (Fig. 1). As an example, S6: Peace (accent), red, made in Korea; S7: Compact, red, made in Japan; S8: Ju-an, red, made in China were differentiated based on the peak intensity, position and patterns. The micro-ATR FTIR spectra for the other 10 seal ink samples are shown in additional information (Fig. SM1). Blind tests were also done to validate the proposed method. Spectra of blind samples stamped by persons who have nothing to do with this project were recorded and queries were done in the database made. The match quality value which indicates the spectral similarity of the reference spectrum to the specimen's spectrum is used to establish the seal ink's identity. The higher the match quality value the better the match. In Fig. 2, a

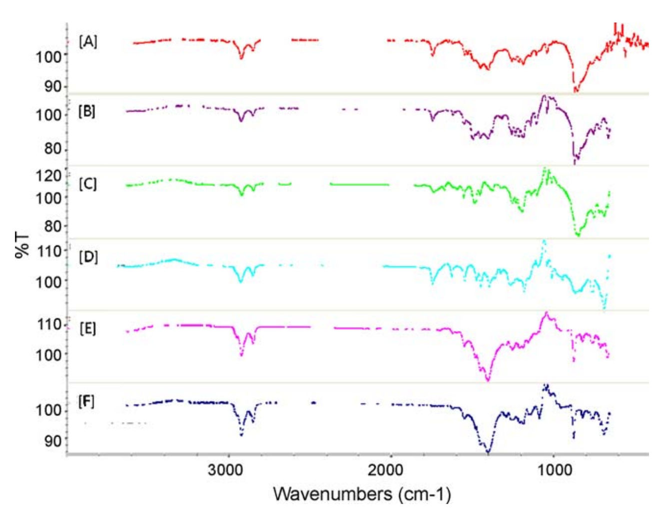

Fig. 2. Blind test result showing micro-ATR FTIR accurately matches unknown sealing paste after running queries in the spectral database. (A) Unknown seal ink sample; (B) a seal ink sample, S2 (match value = 79.19); (C) a seal ink sample, S4 (match value = 54.04); (D) a seal ink sample, S7 (match value = 39.18); (E) a seal ink sample, S3 (match value = 37.63); (F) a seal ink sample, S1 (match value = 37.23).

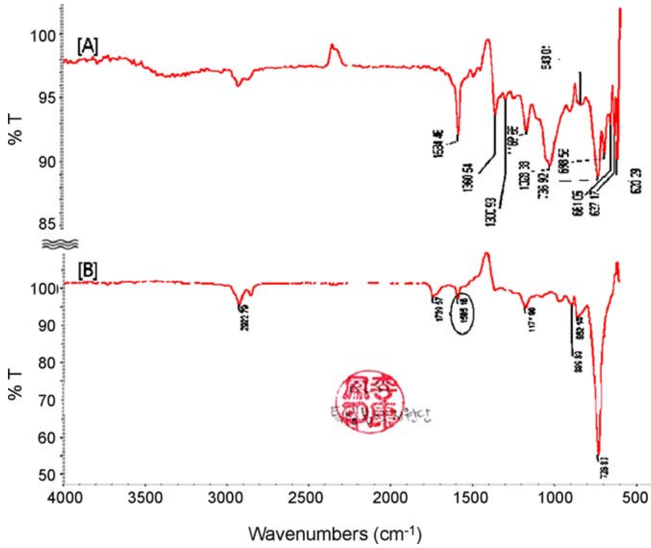

Fig. 3. Spectra of (A) a ballpoint pen and (B) a ballpoint pen on a seal ink.

blind sample (originally S2) was used to test our method. After queries from the database were made, micro-ATR FTIR, accurately identified the seal ink's identity (Korea, Mae Pyo (general); red) based on the highest match value (79.2) among the seal ink. The additional 20 blind test samples were also tested and queries were made. These blind samples were accurately identified the source of seal inks (Fig. SM2).

To validate the proposed methodology, an original document dated 1997 stamped with red sealing ink was analyzed using micro-ATR FTIR and TOF-SIMS. The validation of the TOF-SIMS method was published somewhere [3]. Both analysis results showed that the red sealing ink's chemical composition matches very well with the Mapyo brand.

For a successful determination of the sequence in intersecting lines, the writing/printing material must yield a spectrum that can be resolved from the background. It must also have at least one characteristic band that allows it to be independently imaged. A consistent pattern of results for the two possible line crossing situations (as material A on material B and *vice versa*) should be established [5].

Figs. 3 and 4 clearly show that ballpoint pen ink and seal have spectra that can be resolved from the background, thus satisfying the first criterion. Moreover, the spectra of the ballpoint pen ink (Fig. 3A) shows peak at 1585 and 1170 cm^{-1}, and these peaks are

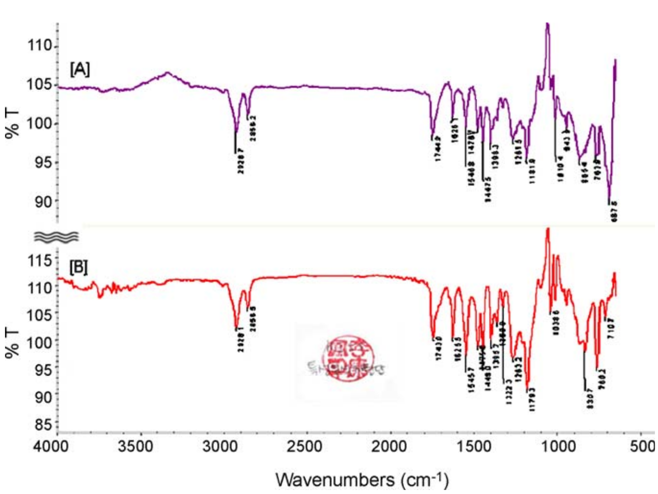

Fig. 4. Spectra of (A) a seal ink and (B) a seal ink on a ballpoint pen.

characteristics of ballpoint pen inks and are attributed to the triarylmethane dyes [4], whereas peaks located at 2928 and 2856 cm^{-1} in Fig. 4A, above are attributed to the C–H stretching from a hydrocarbon backbone in the castor oil, a main component of the seal ink. These peaks can be indicators of the presence or absence of the seal ink or ballpoint pen ink.

Moreover, Figs. 3B and 4B show the micro-ATR FTIR result of ballpoint pen ink on stamped seal ink and stamped seal ink on ballpoint pen ink, respectively. From Fig. 3, the ballpoint pen ink is written over the seal ink, though majority of the peaks are attributable to the seal ink, peak at 1585 cm^{-1}, which is from the ballpoint pen, is distinguishable. However, from Fig. 4, no peaks attributable to the ballpoint pen ink is recognizable, all the peaks can be attributed to the seal ink. We have performed various blind tests with different ballpoint pens and seal inks, and this method can be accurately determined the sequence of intersecting lines (shown in Fig. SM3). Therefore, these data show the apparent usefulness of micro-ATR FTIR in the field of forensic science.

4. Conclusion

Analysis of questioned documents is an important aspect in the forensic field. In this study, the feasibility of using micro-ATR FTIR was shown to be useful in the analysis of documents involving seal inks. The seal inks' origin as well as the sequence of intersecting lines between stamped seal ink and signature with ballpoint pen could be determined using micro-FTIR. It is simple, rapid, non-destructive and it could allow an objective method of analysis that is based on chemical differences inherent to the sample involved.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.forsciint.2010.02.009.

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