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ARTICLES

Nondestructive Classification and Identification of Ballpoint Pen Inks by Raman Spectroscopy for Forensic Document Examinations[1]

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Abstract—As a non-destructive analytical method, Raman spectroscopy often provides insufficient information to identify or differentiate the ink used for the preparation of a questioned document. In this study, blue and black ballpoint pen inks deposited on paper substrate were examined in situ by conventional Raman spectroscopy. Inks were successfully classified based on the total number of prominent bands in Raman spectra. It was found that more than 90% of the samples of the same type and color could be differentiated visually using only Raman spectra, i.e. 94 and 95% for blue and black inks, respectively. As a result of this study, a flow chart has been constructed for blue and black ballpoint pen inks allowing their systematic identification. Raman spectroscopy proved to be a fast and precise technique for forensic ink analysis.

Keywords: questioned documents, Raman spectroscopy, ballpoint pen inks, forensic ink analysis

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Questioned documents, e.g. letters, contracts and insurance claims, are one of the most common types of evidences found in a variety of criminal investigations. Kinds of inks that can be used to prepare a document could be of printers and writing instruments, i.e. gel and ballpoint pens [1]. Compared to gel pens, ballpoint pen inks are still the most commonly encountered ink types by forensic document examiner due to their relatively low prices, wide varieties and availability. As a result, it is important to determine the discrimination power (**DP**) of a particular technique in analyzing pens that are typically sold in a particular country.

Among varieties of analytical techniques, Raman spectroscopy (**RS**) is one of the most preferred techniques due to its several advantages. Firstly, RS can provide the chemical information about the ink rapidly as it does not require any tedious sample preparation steps. Secondly, the integrity of sample as court evidence is preserved as RS is a nondestructive technique [2]. There are quite a number of studies on investigating the forensic application of Raman spectroscopy for inks analysis. Each of those studies use laser sources of different wavelengths, i.e., 514, 532, 633, 685 and 1064 nm [2–6]. Every laser sources has its different pros and cons with respect to the forensic analysis of inks, which is well explained in [7].

On the one hand, DP obtained using conventional RS usually low and high DP tends to be obtained via surface enhanced resonance Raman spectroscopy (**SERRS**), i.e. adding silver colloid to sample and then analyzing via conventional RS. The quality of Raman spectra tends to be improved by SERRS. However, SERRS is less cost-effective than conventional RS as it requires addition of silver colloid onto sample which increased the analysis cost and time [5, 6]. On the other hand, the risk of encountering interference from fluorescence is decreasing as the wavelength of excitation source is increasing. However, ink components that showed weaker Raman activity might not be detected if longer wavelength laser was used [8].

As such, this study aimed to demonstrate the feasibility of Raman spectroscopy as a simple green tool in analyzing 24 types of ballpoint pen inks without involving any complicated statistical techniques or expensive chemicals. The DP of the conventional RS, i.e. FORAM 685 from Foster and Freeman Ltd., in analyzing 24 types of ballpoint pen inks, 12 for blue and 12 for black inks, were determined. Classification flow chart for the pen inks also constructed only based on the features noticeable to the naked eye.

[1] The article is published in the original.

EXPERIMENTAL

Sampling. Samples were prepared by collecting 24 different ink sources (pens); 12 varieties for each of black and blue ballpoint pens. Four different individual pens were sampled for each variety of pens (table). A paper template (Double A premium copy paper, A4 size, 80 gsm, Thailand) was prepared as well. Both pens and paper were brought from UNIKEB located at Universiti Kebangsaan Malaysia, Bangi in Malaysia.

Sample preparation. Ink samples were prepared by drawing a straight line of 5 cm on the paper template. For each variety of pens, every four individual pens were used to prepare five different specimens. As a result, each variety of pens has contributed twenty Raman spectra.

Raman spectroscopy analysis. All analyses were carried out on a Foster and Freeman FORAM 685-2 Raman spectrometer with a 685 nm wavelength laser. The integration time was selected in such a way as to obtain the maximum permissible intensity of peaks. Measurements of spectra were carried out using a 10× objective, applying baseline correction and 100% of the laser power. Each prepared ink sample was examined not later than one-day after drawings were made. The blank paper was also prepared and analyzed in the same manner as the samples and was used as the standard.

All the data analysis was carried out visually. Spectral fingerprinting comparison was used to classify and then differentiate the pen samples. Comparison involved examining the overall pattern of spectra, as well as differences in band positions (presence or absence at specific shift values), band shape (broad or sharp) and relative intensities of adjacent bands. The absolute intensities of the bands were not used because they depend on a number of factors such as laser power and other instrumental effects which cannot be reliably reproduced [9]. Differences in the band location equal to or more than 10 cm^{-1} only considered significant.

With 12 varieties of ballpoint pens, there are 66 possible pen pairs (12 × 11/2 = 66) of blue and black ballpoint pen inks, respectively. After that, DP was calculated using the following equation [10, 11]:

$$\mathrm{DP} = 1 - \frac{2M}{n(n-1)},$$

where M is the number of non-discriminated pairs of samples and n denotes the total number of samples.

RESULTS AND DISCUSSION

Influence of the paper. Figure 1 shows Raman spectra of a blank paper in the range of 300 to 2100 cm^{-1}. The top spectrum is the average of the five spectra that being collected from five different points on a piece of blank paper. A Raman spectrum of blank paper was relatively simple with no significant peaks at all. As such, we will not see any inferences of the blank paper on the Raman spectra of inks.

Preliminary examination of Raman spectrum of pen ink. None of the 24 kinds of pen suffered from fluorescence interference. For every 24 kinds of pen inks, four different individual pens were purchased to provide information on the intra-variation of a particular pen inks. For each individual pen, five Raman spectra were acquired from five points on a single line that was prepared by that particular individual pen. Then, an averaged Raman spectrum was calculated from that five Raman spectra. In brief, Raman spectra showed good repeatability, as seen in Fig. 2, which showed a mean Raman spectrum of BC2 that calculated from five Raman spectra obtained from a particular individual pen. It has been noted that the positions, shapes and relative intensities of the major bands from four different individual pens were highly similar. Therefore, the pen inks were classified and then discriminated based on the mean Raman spectrum.

Raman spectrum of pen ink. In general, all blue and black pen inks did not showed obvious different spectral features, except Papermate black pen inks and Pilot blue pen inks. On the one hand, black pen inks showed highly similar Raman spectra profiles, i.e. a broad band of intermediate intensity. Both models of Papermate black pen inks exhibited the highest number of bands in Raman spectra, i.e. seven bands. The other pen inks showed exactly only four main Raman bands that appeared quite similar with each other.

In contrast, blue pen inks only exhibited much less number of main Raman bands, i.e. 1–3 bands, except both models of Pilot pens that showed more than five main Raman bands. Most of the Raman bands of blue pen inks appeared to be broad and short. While Pilot pens produced sharp Raman bands of relatively high intensity, as shown by Fig. 2.

Classification and discrimination of the pen inks. The Raman spectra of 24 kinds of ink entries were recorded. It was noted from the obtained 24 spectra that there were some similar features for these spectra. For both blue and black pen inks, the total number of main Raman bands was used to classify the pens to different groups. After that, a group that composed of most number of members was sub-divided based on the presence of selected main Raman band within few pre-defined wavenumber regions. Lastly, the attempt

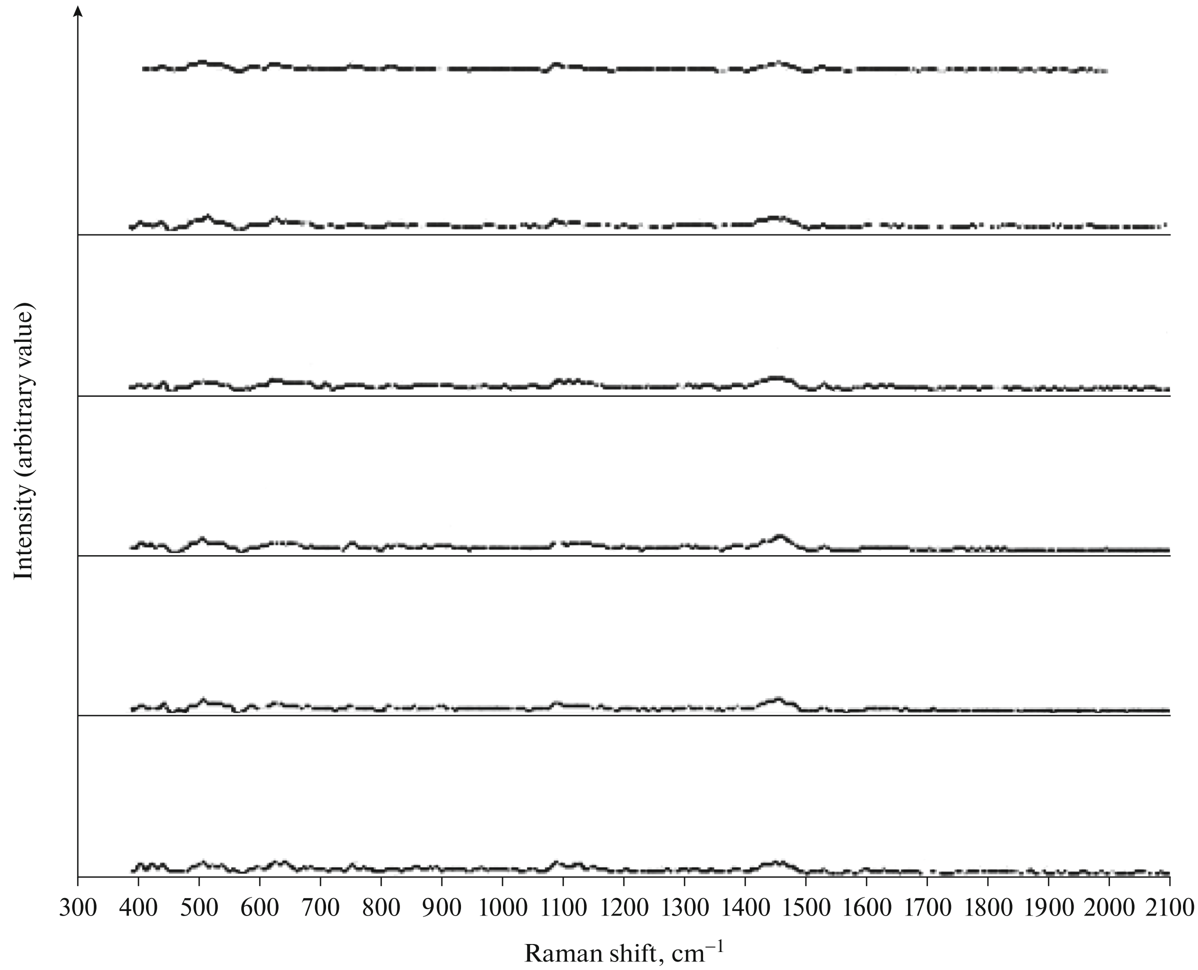

Fig. 1. Raman spectra of blank paper. The mean Raman spectrum of blank paper (top) was calculated from Raman spectra collected from five different points of a piece of paper.

of differentiation was done based on the presence of particular minor bands within a selected region or absolute positions.

In general, the twenty-four ink entries were classified to three and two main groups for blue and black inks, respectively, according to the total number of main Raman bands. For both pen inks, group one was further subdivided into three different sub-categories, respectively. Figure 3 illustrates the flow charts constructed on the basis of the visual comparison of bands in the Raman spectra, for blue (Fig. 3a) and black pen inks (Fig. 3b). The first criterion used to classify the 12 pen types was the total number of observed prominent bands in Raman spectra. For instance, blue ballpoint pen inks could be divided into three different groups, i.e. group one comprised of seven pen types which all only showed a single prominent band in Raman spectra. After then, group one for blue and black pen inks, respectively, was divided into three sub-groups by the wavenumber regions to which the absolute location of a selected prominent band belongs.

A flow chart was successfully constructed for the blue pen inks. It was able to differentiate both models of a single brand, i.e. Faber-Castell, G'soft, Papermate and Stabilo. On the other hand, both models of Bic and Pilot pens could not be differentiated from each other. Though the two models of Papermate (BE1 and BE2) could be discriminated from each other, each of them could not be differentiated from Faber-Castell (BE1 and BA1) and G'soft (BE2 and BD2). Thus, the discriminating power was equal to about $(62/66) \times 100 = 94\%$.

For black ballpoint pen inks, the proposed flow chart divided the 12 inks into two main groups. Among the six studied pen brands, only both models of LTC and Zebra could not be differentiated from each other. One of the Stabilo pen's models (HD2) was not differentiated from G'soft pen (HE1). As a result, 63 out of

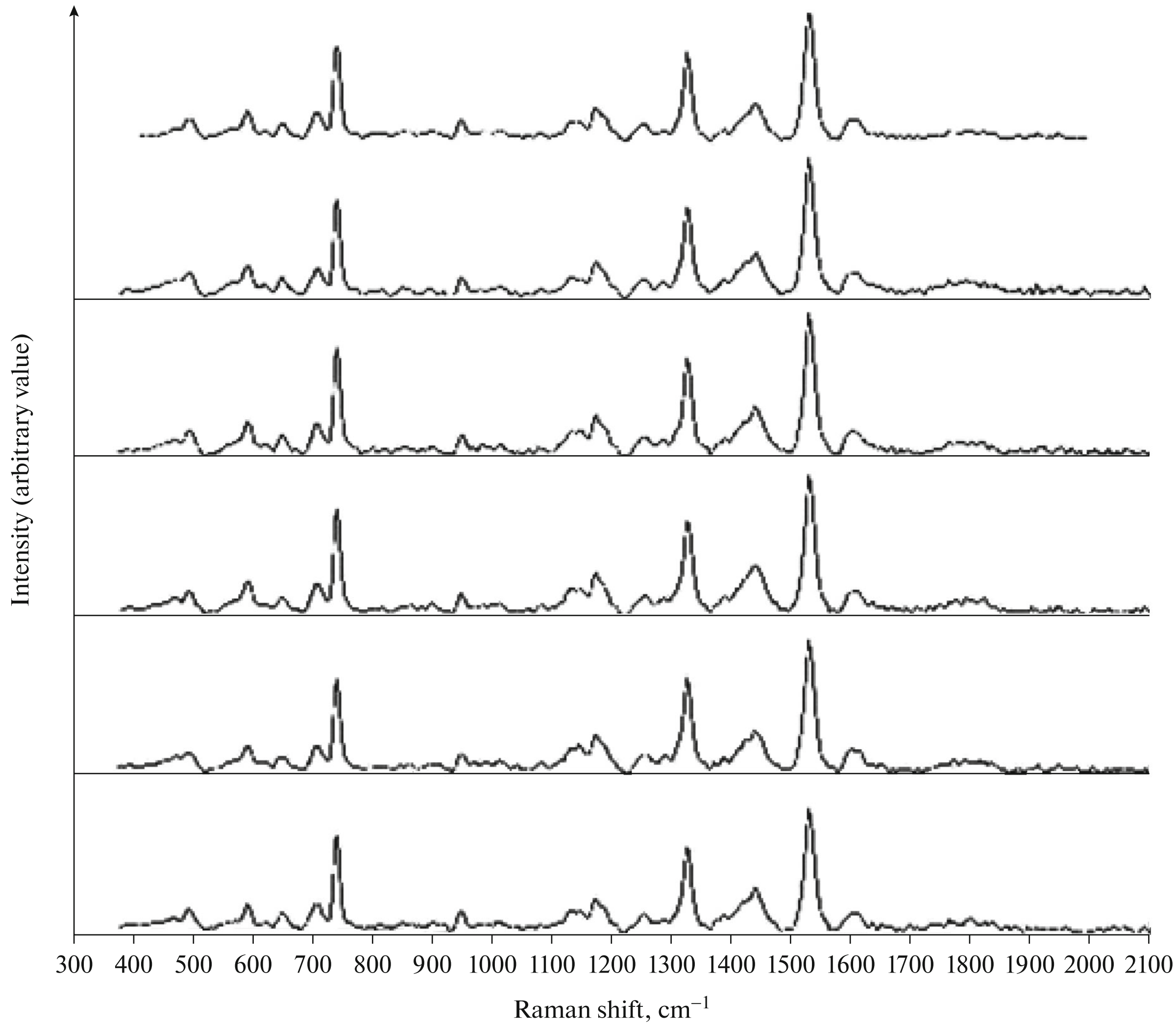

Fig. 2. Example of reproducibility of the Raman spectroscopy for ink analysis. The mean Raman spectrum of sample BC2 (top) that was calculated from five Raman spectra (of five different specimens prepared using one of the four individual pens).

Details and identification number of each selected varieties of black ballpoint pens (each variety of pens was assigned with an identification number, ID no.)

Blue ballpoint pen inks		Black ballpoint pen inks	
label	pen model	label	pen model
BA1	Faber-Castell BP 1423 1.0	HA1	Paper Mate Kilometrico M
BA2	Faber-Castell Grip X7	HA2	Paper Mate Kilometrico F
BB1	Bic RS2 F	HB1	Faber-Castell Ballpen 1423 1.0
BB2	Bic Round Stic F	HB2	Faber-Castell Clickball 1422 0.7
BC1	Pilot Super-GP 1.0	HC1	LTC BP-BG-Z8 F
BC2	Pilot Super Grip F	HC2	LTC Ballpen BG828 SF
BD1	G' soft GS-7.7	HD1	Stabilo Liner 808 F
BD2	G' soft GS-BP-X5 XF	HD2	Stabilo Galaxy 818 M
BE1	Paper Mate Inkjoy 100RT F	HE1	G'soft R200 Semi Fine
BE2	Paper Mate KV2 M	HE2	G'soft GS-BP-X5 XF
BF1	Stabilo Liner 308 F	HF1	Zebra Z-2 0.7
BF2	Stabio Excel 828 F	HF2	Zebra Z-1 S

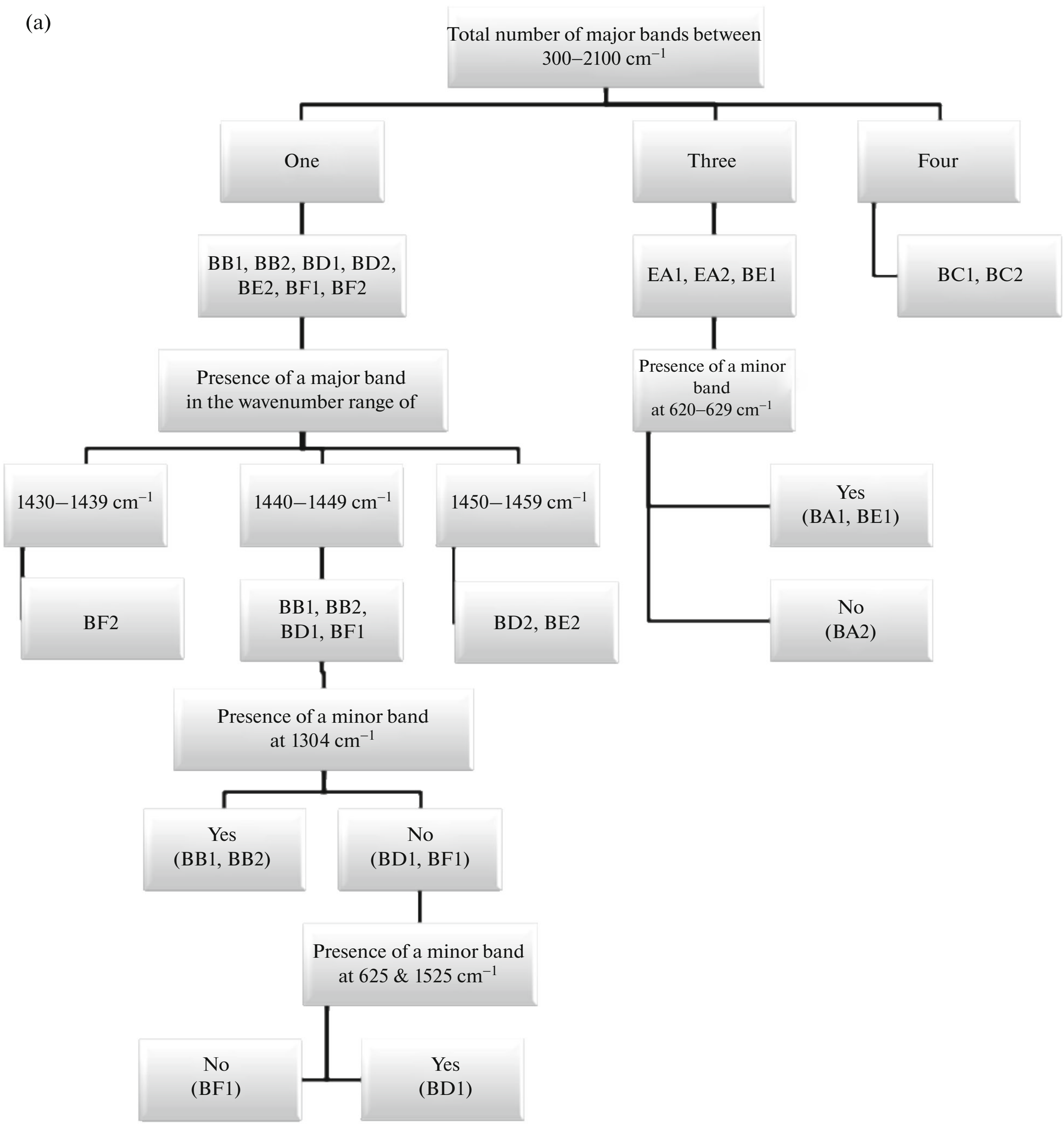

Fig. 3. The classification flowchart, according to prominent bands in the Raman spectra, for the blue ballpoint pen inks (a) and for the black ballpoint pen inks (b) analyzed.

the 66 pen pairs could be discriminated. In other words, the discriminating power was 95%.

A non-destructive approach to the discrimination of ballpoint pen inks on paper has been developed based on the Raman spectroscopic technique. The ink entries collected from various manufacturers, or brands were classified into few main groups and several subgroups according solely to the Raman spectra and presented in flowcharts. The discrimination power was calculated to be above 90%. This approach is a non-destructive, rapid and practical tool to differentiate and identify the ink entries on documents.

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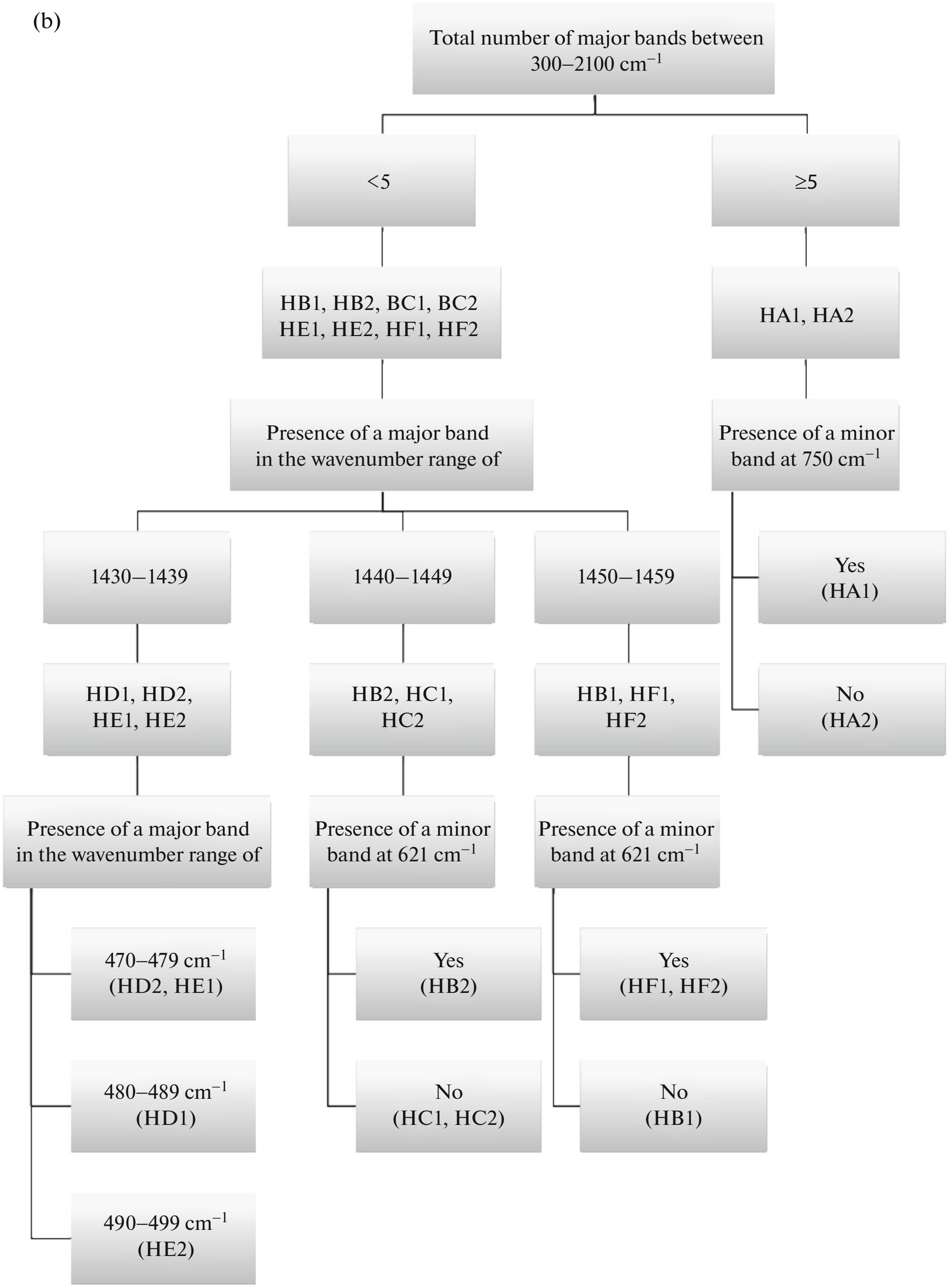

Fig. 3. (Contd.)

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