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Statistical Discrimination of Blue Ballpoint Pen Inks by Infrared (IR) Spectroscopy

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ABSTRACT

Statistical chemometric method was used in discriminating 24 blue ballpoint pen inks from six different brands (Pilot, Carera, Stabilo, Faber-Castle, G-soft and Papermate) available in Malaysian market. Discrimination method was developed based on the combination of infrared spectra (IR) and chemometric technique which comprise of principal component analysis (PCA) and Agglomerative Hierarchical Clustering (AHC). The chemometric software used was XLSTAT 2011. The spectral region 4000–400 cm^{-1} was used to 'fingerprint' each ink from the 24 samples. PCA was used to detect any outliers whereas AHC was used to separate the ballpoint pen inks into their own class. This study showed that acceptable statistical discrimination (70.92% correct classification of the ballpoint pen dataset) between these 24 samples. FTIR-PCA and FTIR-AHC were successfully discriminate three different brands which were Carera, Pilot and g-soft. While, the other three brands, Papermate, Fabercastle and Stabilo could not be discriminated perfectly. The results of this study indicate that Transmission FTIR Spectroscopy coupled with chemometrics is useful discriminating tool for forensic studies involving inks.

| Blue ballpoint pen inks| PCA | AHC| FTIR |

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1. INTRODUCTION

Since ancient times, various writing instruments have been used for writing process. Nowadays, quill and nib pens have given way to other classes of writing instruments such as the ballpoint, roller ball and gel pens which have different requirements for the properties of their writing inks [1]. This study emphasizes on ballpoint pen inks available in Malaysian market as these pens are often used in the occasion of signing important documents. Although all blue ballpoint pen inks may look the same, there can be some important differences in their chemical composition, constituent and substances. Modern inks contain many substances aiming to improve ink characteristic [2].

The examination of inks is often performed to differentiate between inks in order to evaluate the authenticity of a document. Its application regards the detection and confirmation of alteration to documents with significant financial value like checks, insurance claims, wills, contract and tax return [3].

A ballpoint pen ink consists of synthetic dyes in (acidic and/or basic), pigments (organic and/or inorganic) and a range of additives [9].

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Inks of similar color may consist of different dye composition and are frequently the subjects of forensic examinations. Over recent years, technological developments have rapidly expanded the range of pen designs and ink composition used throughout the world [4].

The inks can be discriminated by non-destructive or destructive methods [2, 5] depending on whether a sample needs to be taken from the document, a process that would alter it. The destructive methods such as High Performance Liquid Chromatography (HPLC), Thin Layer Chromatography (TLC), Capillary Electrophoresis (CE) and Gas Chromatography/Mass spectroscopy (GC/MS) [1, 2, 5]. The non-destructive methods are Scanning electron microscopy (SEM), Video Spectral Comparative (VSC) and Raman Spectroscopy [2, 5, 6]. However, these techniques are complex and require a long time consuming analytical steps [7]. Besides that, it's requiring very expensive instrument [6].

In this study, Transmission FTIR Spectroscopy was chosen as a technique for inks analysis although it is destructive method due to cost effectiveness, good signal-to-noise ratio (absorb 100% energy) and it can produce the best quality of the spectrum.

However, it is difficult to discriminate the pen inks and errors become occur when analyze the IR data manually [8]. As alternative, the data obtained from this technique may be further analysed using chemometric methods because the employment of multivariate analysis allows the extraction of more information based on t he

similarities and differences among samples in a d ataset [10].

This can be demonstrated by the application of chemometric techniques using Principle components analysis (PCA) and Agglomerative Hierarchical Clustering (AHC) to the chromatographic or spectral data.

These chemometric methods are based on the computer programming or database. The chemometric software used to perform PCA and AHC on the data was XLSTAT 2011. It is used to investigate the measurable variability between the same colors of pens with different brands by matching of an ink to the database of chromatograms. This technique shows quantitative analysis [4].

2. EXPERIMENTAL

2.1 Materials, chemicals and instrument

Analysis was performed for 24 bl ue ballpoint pen inks with various brands, commonly available in Malaysia. The chemicals were involved are acetone and Potassium Bromide (KBr) powder (J. T. Baker, USA). The beaker, spatula, syringe (Terumo, Philippine), pallet plate, handy press (Thermal Scientific USA) and crystal mortar was used in the pallet making process. Infrared spectra (IR) were recorded with the use of a Transmission FTIR spectrometer (Thermo Nicolet 6700 FTIR). Transmittance was measured from 4000 t o 400 c m^{-1}. Before starting a measurement a b ackground spectrum was recorded. The transmittance values were normalized to the range 0–1.

2.2 Sampling

24 blue ballpoint pen inks were purchased from several Stationary shops in Shah Alam. All the pen samples divided into their characteristic and classification. The sample identification for blue ballpoint pen inks is shown in Table 1.

2.3 Sample preparation

Small amount of blue pen ink was transported from the ink barrel of each pen using a syringe (Terumo, Philippine). The ink was then mixed and ground together with the Potassium Bromide (KBr) powder (J.T. Baker, USA) in a crystal mortar (Thermal Scientific, USA) until it becomes homogeneous. Every steps of the sample preparation need to avoid water moisture since it will interfere the spectrum with hydroxyl (OH) peak. After grinding, a hand presser (Thermal Scientific, USA) was used to pressed the powdered mixture and obtain a suitable pellet for analysis.

Table 1 Sample identification for blue ballpoint pen inks.

No	Brands / Types	Sample
1	Carera B3-II	CbB11
2	Carera B7 Fine	CbB21
3	Carera B8	CbB31
4	Carera Fornine 88	CbB41
5	Faber Castle Clickball 1422 Fine	FbB11
6	Faber Castle Roller S-Fine	FbB21
7	Faber Castle Ballpen 1423 Fine	FbB31
8	Faber Castle Ballpen 1423 S-Fine	FbB41
9	Papermate Kilometrico Medium	PMbB11
10	Papermate A1	PMbB21
11	Papermate Propel	PMbB31
12	Papermate Image	PMbB41
13	Stabilo Liner 308	SbB11
14	Stabilo Excel 828 F-Needlepoint	SbB21
15	Stabilo Marathon	SbB31
16	Stabilo Galaxy 818 X-Tra Fine	SbB41
17	G-Soft Ballpoint Pen	GbB11
18	G-Soft R200 Semifine	GbB21
19	G-Soft Gs-Bp-R6 Medium	GbB31
20	G-Soft R100 Fine	GbB41
21	Pilot Super-Gp	PbB11
22	Pilot Supergrip F	PbB21
23	Pilot Rexgrip	PbB31
24	Pilot Supergrip M	PbB41

2.4 IR analysis of the blue ballpoint pen inks

The pallet was analyzed by Transmission FTIR spectrometer. IR spectra in the mid-infrared spectral range (4000-400cm^{-1}) were recorded in the transmission mode. Each spectrum represented a collection of 32 scans for each.

2.5 Chemometric analysis of the IR spectral data

The selected wavenumbers for each sample were subjected to the principal component analysis (PCA) and Agglomerative Hierarchical Clustering (AHC). In this study, the XLSTAT 2011 software package was employed for multivariate statistical calculations.

3. RESULTS & DISCUSSION

3.1 Differentiation of elemental composition

Determination of the elemental composition of blue ballpoint pen ink has been very useful in the characterization of inorganic pigments and organic dyes. Observation of infrared fluoresce of the ink was done by illuminating the pen ink with visible radiation and then induced fluoresce was detected by means of filters and infrared sensitive film. The effect was to convert infrared to visual equivalent. For the differentiation of inks by the infrared spectra, the peak positions and relative intensities should be analyzed [9]. The infrared spectra for the six different brands with four different type of blue ballpoint pen inks were analyzed in the region between 4000-400 cm^{-1} as shown in figure 1.

Therefore, the infared data was divided into group also called functional group according to position of peak, wavelength and intensity. As we can see, infrared data was produced many groups of the peak where some of peaks were presented in the all brands of pen inks and some of peak may not. The discrimination process of blue ballpoint pen inks and their elemental composition can be done by observing the position of peak and their wavenumber.

Based on the observation, most of peaks were presented in the all brands of pen inks. Means that, most of pen inks have the same element composition.

According to these peaks, it is indicate that, the manufacturers for all brands which are Carera, Faber-Castle, Papermate, G-soft, Stabilo and Pilot might be using the same ingredient where every peak present in all pen inks. Therefore, these peaks unusefull in order to discriminate the pen inks. The best discrimination occurred when the peaks presented significantly different from the other pen inks peak. However, the problem also occurred when only few different peaks were observed and also occurred at the other pens.

In addition, this is particularly true for the IR data where it would be almost impossible to distinguish between pens manually [8]. In a nut shell, the limitation of information which is only few different wavenumber observed and the way to analyze the IR data manually makes it difficult discriminate the pen inks.

In this study, multivariate chemometric techniques which are Principle Components Analysis (PCA) and Agglomerative Hierarchical Clustering (AHC) were used as alternative techniques in order to discriminate the pen inks statistically and specifically. These techniques require more than five wavenumber or variables.

After selection process of the position peak at different wavenumber, only fourteen possible and relevant peaks were choosing after eliminate the peak that commonly present in the most pen. All the fourteen peaks that were selected representative the different functional group. The possible and relevant functional groups that were selected are shown in the table 1.

3.2 PCA and AHC analysis

The chemometric software used to perform PCA and AHC on this data was XLSTAT 2011. XLSTAT 2011 does not allow more than three hundred variables and not less than five variables to be used in any of its analyses. Infrared spectra provide many wavenumber or variables. After selection process of the position peak at different wavenumber, only fourteen possible and relevant peaks were choosing after eliminate the peak that commonly present in the most pen.

Therefore, some of variables would have to be removed for the dataset to comply with the XLSTAT 2011 limitations. Feature reduction of this kind can be achieved by performing a cluster analysis on the variables over the pen ink samples. According to this technique, variables carrying similar information about the pen ink samples are expected to form clusters from which the most representative variables can be chosen.

In the first place, PCA was necessary for the removal of any outliers in the data. The presence of the outliers can affect the results of the AHC through an overestimation of the within sample variance, something that can reduce the effectiveness of the discriminal model. Although the deletion of some data may appear to introduce bias in the analysis, in this case, such a p rocedure was necessary since for each brand has four pens were of the same batch and their spectra were expected to come from the same population.

In multivariate systems, PCA can aid the observation of outliers by projection of the data on a plane after Varimax rotation of the first two extracted components (F_1 and F_2). The next step in the study regarded the quality of the discriminant model calculated in AHC.

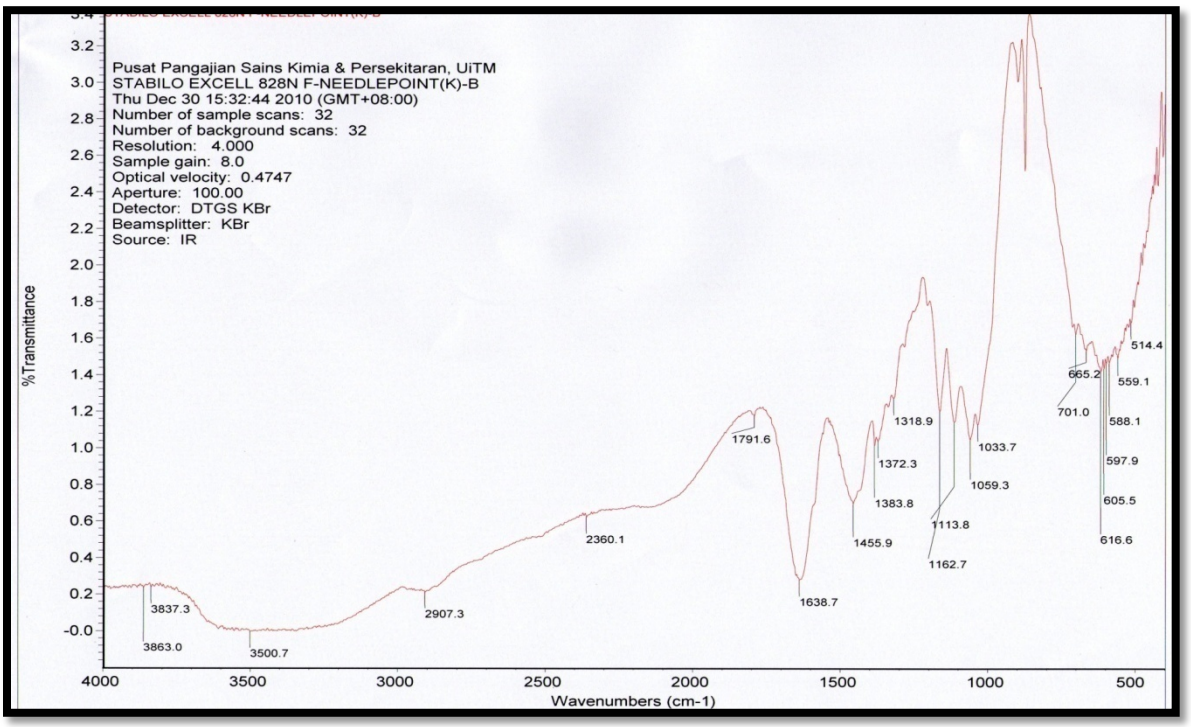

Fig. 1 IR spectra of blue ballpoint pen ink.

Table 2 The possible and relevant wavenumber with their functional groups.

No.	Wavenumber (cm^{-1})	Types of bond	Functional group
1	3061	H-C=C-H	Alkenes
2	3029	C-H	Aromatic ring
3	2870	C-H	Alkanes
4	2360	-	-
5	2342	-	-
6	1526	C=O	Aldehyde, ketones,carboxylic acids,ester
			Aromatic ring
		C=C	
7	1724	C=O	Carbonyl group
8	1666	H-C=C-H	Alkenes
			Aldeydes, ketones, carboxylic acids,ester
9	1412	H-C=C-H	Alkenes
10	1345	NO_2	Nitro compound
		C-N	Amines, amides
11	1274	C=O	Aldeydes, ketones, carboxylic acids,ester
12	1219	C=O	Aldeydes, ketones, carboxylic acids,ester
13	1156	C-N	Amines, amides
		C=O	Aldeydes, ketones, carboxylic acids,ester
14	723	H-C=C-H	Alkenes

3.3 Classification of blue ballpoint pen inks by FTIR-PCA and FTIR-AHC

In this study, fourteen possible and relevant wavenumber or Infared data (in table 1) were used after. The classification of blue ballpoint pen inks was studied individually at each of the fourteen wavelengths or variables and using a combination of all these wavelength simultaneously, with two chemometric algorithms, PCA and AHC.

After selection all these fourteen data, the shape of peak were observed at that wavenumber and then coding it based on several factors. Firstly, we need to observe the strength of the peak whether it is strong or medium. Secondly, observed whether the peak may or may not occur in the other pens. Therefore, three values were used in order to representative all the wanumber according to these factors. These values are 10, 5 and 2. The wavenumber that has strong peak was coded with value 10. Then, value 5 represents as the medium peak and also that peak only occurred at their pens while value 2 for the pens that do not have the mention peak. All the coding data were used as the PCA and AHC variables. The PCA score plot showing the separation of ink classes is shown in the table figure 2.

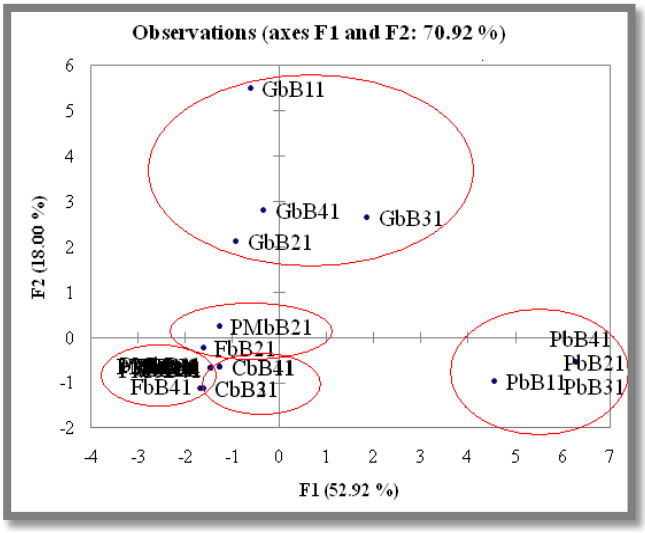

Fig. 2 Score plot of F1 vs. F2.

Based on the data obtained, PCA analysis can discriminate 70.92 % of the blue ballpoint pen inks. PCA analysis led to complete separation about fifteen of blue ballpoint pens, leaving remaining nine blue ballpoint pens which assembly in one group as can seen from the table 5. The best discrimination was obtained for all types of pens from brands Carera (CbB), G-soft (GbB) and Pilot (PbB) which completely separated from all the other pens.

The CbB11, CbB21, CbB31, and CbB41 remained significantly separated from the brands Pilot, G-Soft, Papermate, Stabilo and Faber-Castle where Carera pens performed in one group.

Means that, the characteristic of pens from brand Carera slightly different from the other pens. From the data obtained, CbB31 and CbB2, are pointed at the same point while the point for CbB11 same the point of CbB41. Although same brands, all Carera pens might have different characteristic and constituents to each other in their group. However, they are still closer to each other and still can performed in one group in order to discriminate with the other pens. PCA analysis also very useful to separate and discriminate different types of pens within same brand. Therefore, one of the six brands successfully separated and can discriminate from other brands.

Other than Carera pens, Pilot and G-Soft pens also completely separated from the other pens into their own group. The four types of Pilot pens performed in this study are PbB11, PbB21, PbB31, and PbB41. As we can see, the Pilot Super-GP (PbB11) pen was separated from the other pens in their groups because it have different characteristic than the other three pens which are Supergrip-F(PbB21), Pilot Supergrip-M (PbB41) and Pilot Rexgrip (PbB31). These three types of Pilot pens have the same characteristic due to pointed at the same point. As Carera pens, all Pilot pens performed in one group, means that their characteristic might be same and close to each others.

The G-soft pens showed significantly discrimination from other pens. The various g-soft pens performed are GbB11, GbB21, GbB31 and GbB41 where assembly in one group.

PCA analysis showed that all types of G-Soft pens have different characteristics to each other because all g-soft pens performed in different point. Means that, manufacturer used different ingredient to make these pens.

The three brands of pens were misclassified into their own group as belonging to other classes as shown in figure 2. These three brands of pen which are Fabercastle, Papermate and Stabilo were classified into one group except FbB21, FbB41 and PMbB21. However, in the PCA result, Faber Castle FbB21 and PMbB21 were classified into one group. Then, we still can discriminate both pens from the other pens. In a nut shell, FbB11, FbB31, PMbB11, PMbB31, PMbB41, SbB11, SbB21, SbB31 and SbB41 have the same characteristic except FbB21 was well separated from the other pens although classified in same group.

After PCA analysis was performed, the AHC analysis was took place for the confirmation purpose. The result that produced by AHC analysis was performed in the figure 3 (AHC separation of IR blue ballpoint pen samples).

AHC is multivariate chemometric technique which produced result by class or cluster. In this study, the result that performed by AHC very similar with the result performed by PCA. Based on the data obtained, all from brands Carera which are CbB11, CbB21, CbB31 and CbB41 were classified into one class which is C1. The blue ballpoint pens from Carera were completely separated from the other brands of pens. Therefore, Carera pens have their own characteristic and elemental composition where the other brands of pens do not have it. We can conclude that, manufacturer of Carera pens was used their own formula

and ingredient in order to make these pens, so their pens are significantly different from the other brands of pens. Then, the three brands which misclassified into their own group in PCA analysis were assembly into one class which is C2 in AHC analysis. These three brands are Fabercastle, Papermate and Stabilo. However, two pens from different brands which are FbB21 and PMbB21 were classified into one class which is C3. Therefore, most of pens from Fabercastle, Papermate and Stabilo except FbB21 and PMbB21 have the same characteristic and elemental composition since the manufacturer from these brands were slightly used the same ingredient to make it and the intensity of pens also same. FbB21 and PMbB21 do not included into C2 because they have their own characteristic.

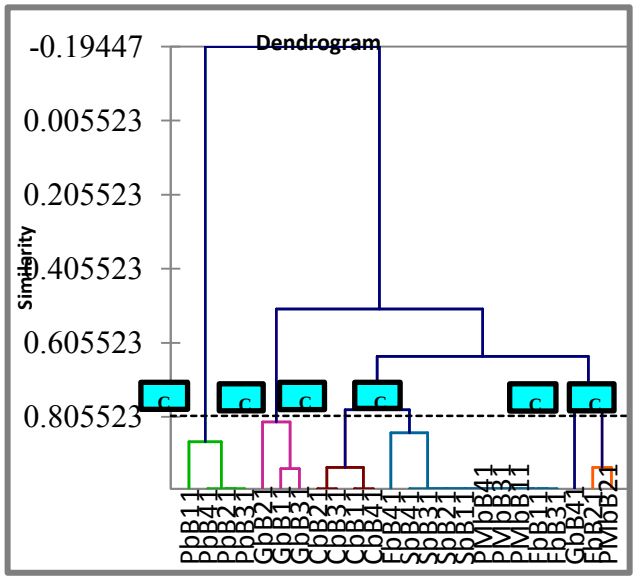

Figure 3 : Dendrogram of clustering of inks based on IR data

For G-soft pens, by using AHC analysis, only three types of pens were classified into the same class which C4 and these pens are GbB11, GbB21 and GbB31.

The other one is GbB41 which not classified with the other three pens but it is classified into their own class which is C5. The last brand is Pilot which successfully classified into their owns class which is C6. The Pilot pens also have their own characteristic and elemental composition since it i s significantly separated from the other brands.

The three types of blue ballpoint which are FbB21, PMbB21 and GbB41 exit from their own brands of class because all these three pens have a peak at wavenumber 723 cm^{-1} and PMbB21 have extra peak at wavenumber 1526 cm^{-1}. These two types of peak are not presented in the other pens so, that's why these three pens were separated into their own class. However, GbB41 was excluded from FbB21 and PMbB21 class due to their peak presented at 723 cm^{-1} is very small as compared to the other two pens. The functional group presented at wavenumber 723 cm^{-1} is alkenes groups (-C=C-) while at 1526 cm^{-1} is C=O (ketones) and aromatic ring group (C=C).

Based on this study, we can conclude that although all the ballpoint pens have the same color which is blue, by the naked eyes they may look same but actually every brand of pens have their own characteristics and elemental composition.

By using PCA and AHC, we can see three different brands which are Carera, Pilot and g-soft are successfully separated from the other pens. In addition, most of pens have the same basic composition which is resins, dyes and volatile components. Ballpoint pen is a quick-drying paste aqueous solvent and not aqueous solvent.

Therefore, the manufacturer of Carera, Pilot and g-soft may have extra or special ingredients to produce their pens, so they are different from the other. However, some of pens were misclassified due to their manufacturer may used only the basic ingredient without using any special ingredient in order to discriminate their pens from other pens.

4. CONCLUSION

It has been proved that the feasibility of using infrared (IR) spectroscopy which is Transmission FTIR spectroscopy was shown to be useful in the analysis of documents involving ballpoint pen inks. This study showed that acceptable statistical discrimination (70.92% correct classification of the ballpoint pen dataset) between twenty four of blue ballpoint pen inks of different brands and types could be achieved by examination of infrared spectroscopy with the application of a multivariate chemometrics protocol for the analytical data. This is particularly true for the IR data where it would be almost impossible to distinguish between pens manually [8].The IR data were visualized as a pattern in multivariate space using chemometric techniques which are Principle Components Analysis (PCA) and Agglomerative Hierarchical Clustering (AHC). The chemometric software used to perform PCA and AHC on this data was XLSTAT 2011. In this study, classification of blue ballpoint pen inks by FTIR-PCA and FTIR-AHC indicate that they were successfully discriminate three different brands of blue ballpoint pens which are Carera, Pilot and g-soft from the other brands. While, the other three brands, Papermate, Fabercastle and Stabilo could not be discriminated perfectly. The results of this study indicate that Transmission FTIR spectroscopy coupled with chemometrics can be more powerful discriminating tool for forensic investigator to investigate the cases involving inks.

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REFERENCES

[1] Williams, M.R., Moody, C., Arceneaux, L.A., Rinke , C., White, K., Sigman, M.E., (2009). Analysis of black writing ink by electrospray ionization mass spectrometry. *Forensic Science International, 191*, 97-103.

[2] Thanasoulias, N.C., Parisis, N.A., Evmirids, Nicholaos P., (2003). Multivariate chemometrics for the forensic discrimination of blue ball-point pen inks based on their Vis Spectra.*Forensic Science International, 138*, 75-84.

[3] Djozan, D., Baheri, T., Karimian, G., Shahidi, M., (2008). Application of the micro–FTIR spectroscopy, Raman spectroscopy and XRF method examination of inks. *Forensic Science International, 158*, 164-172.

[4] Adam, C.D., Sheratt, S.L., Zholobenko, V.L., (2008). Classification and individualization of black ballpoint pen inks using principle component analysis of UV-vis absorption spectra. *Forensic Science International,174*, 16-25.

[5] Dirwono, W., Park, J.S., Agustin-Camacho, M.R., Kim, J., Park, H-M., Lee, Y., Lee, K-B., (2010). Application of micro-attenuated total reflectance FTIR spectroscopy in the forensic study of questioned documents involving red seal inks. *Forensic Science International, 199*, 6-8.

[6] Senvaitiene, J., Beganskiene and Kareiva, A., (2005). Spectroscopic evaluation and characterization of different historical writing inks. *Vibrational Spectroscopy*, 37, 61-67.

[7] Gallidabino, M., Weyermann, C., Marquis, R., (2010). Differentiation of blue ballpoint pen inks by positive and negative mode LDI-MS. *Forensic Science International, 6103*,10 [8]M. Hu, K. Kransz, J. Chen, G. X. Jun, J. Li, and H. Gelboin, Drug Metabolism and Disposition, 31 (2003), 924-931.

[8] Kher, A., Mulholland, M., Green, E., Reedy, B., (2006). Forensic classification of ballpoint pen inks using high performance liquid chromatography and infrared spectroscopy with principal components analysis and linear discrimin ant analysis. *Vibrational Spectroscopy, 40*, 270–277.

[9] Denman, J. A., Skinner, W.M., Kirkbride, K..P., Kempson, I.M. 2010. Organic and inorganic discrimination of ballpoint pen inks by ToF-SIMS and multivariate statistics. *Applied Surface Sci.* **256** :2155–2163.

[10] Panero, F.S. and da Silva, H.E.B. 2008. Application of exploratory data analysis for the characterization of tubular wells of the North of Brazil. *Microchemical Journal*, **88**, 194–200.