

and whitish glowed samples as ballpoint pen and gel pen inks, respectively. It was also important to note that the luminescence characteristic of a pen was not determined by the types of pens. In this study, both ballpoint and gel pen inks might luminesce.

Attenuated total reflectance- Fourier transform infrared spectroscopy

Through ATR-FTIR spectroscopy, complex interacting vibrations were observed in the 'fingerprint' region ($1800-600\text{ cm}^{-1}$). It is worth noting that no attempt was made to predict the compounds since the aim of this study is to relatively compare the ATR-FTIR spectra to establish the possible similarities among the ink samples. Figure 2 illustrates the general pattern of ATR-FTIR profiles of representative pen inks. ATR-FTIR spectra patterns of the ink samples were observed to be different, particularly between the different types of pen inks. Detailed comparison demonstrated the variations in the respective ATR-FTIR profiles even though the ink samples were originated from the same types.

For more objective comparison, the data points of ATR-FTIR spectra were normalised to the total area of the spectrum to correct the multiplicative scaling effect and subjected to PCA, in a situation where information on ink sample classification is needed, such as to investigate unknown origins of ink samples. Figure 3 illustrates the score plot generated through PCA. Note that the score plot was developed with the first two PCs, accounting for 76.9% of the explained variance. Generally, two main clusters of ink samples were evident in the score plot. Cluster A was mainly constituted by ballpoint pen ink samples, and Cluster B mainly consisted of only gel pen ink samples. Note that there were two gel pen ink samples (i.e., GP03 and GP04) found to be located within Cluster A with a majority of ballpoint pen ink samples. In other words, these two samples could have contained composition more similarly to ballpoint pen inks.

Through PC1 (56.3%), it was observed that three samples (i.e., BP01, BP09 and GP02) were justified to

be away from the two main clusters, where one sample located at the left upper quadrant and the other two situated at the left lower quadrant of the score plot. On the contrary, samples in Cluster A showed positive score while those in Cluster B reported with the negative score on PC2 (20.6%). It is possible that closely located samples in the respective clusters could have produced from very similar ingredients.

Duplicate samples, namely GP10a and GP10b as indicated by the dotted line, were located very closely in the score plot to suggest the distance between two points that could be arisen from the same sample. Samples, such as BP03 and BP04, which were also very close to each other, therefore could not be differentiated through the score plot, possibly due to their very similar ink compositions between samples. Note that only the first two PCs were considered and interpreted in this study, where PC3 (9.2%) did not demonstrate any influence over the separation in PCA.

Thin layer chromatography

The solubility of ink samples in methanol was investigated before TLC, where 13 samples were found soluble in methanol. Of these samples, 10 were the ballpoint pens while three were gel ink samples, namely GP02, GP03 and GP04. It is interesting to find that these three ink samples were luminesced under VSC observation, distinguishing them from other gel pen inks. It was also noted that they were clustered closer to the cluster consisting of ballpoint pen inks in ATR-FTIR score plot. Conventionally, only dye-based inks are found soluble in methanol while pigment-based inks previously found in gel pens are generally insoluble [7, 22, 23]. Gel pens made up of pigments are reported to be more resistant to strong organic solvents [4]. Our results showed that the three ink samples with different observations could be made up of dye, although they exhibited gel pen ink characteristics upon writing and marketed as gel pens. Table 3 shows the outcome upon TLC using two different solvent systems on 13 methanolic samples.