DIFFERENTIATION OF GEL PEN INKS BY USING HIGH PERFORMANCE THIN LAYER CHROMATOGRAPHY AND GAS CHROMATOGRAPHY-MASS SPECTROMETRY

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ABSTRACT: The present study aims to distinguish the blue, black, red and green gel pen inks on the basis of their chemical constituents using High Performance Thin Layer Chromatography (HPTLC) and Gas Chromatography-Mass Spectrometry (GC-MS). HPTLC found suitable for studying dye base gel pen inks whereas GC-MS was used for both pigment and dye based gel pen inks. Interpretation of results was done on the basis of major components followed by minor components present in an ink sample. Maximum differentiation was achieved by the minor components as compared to major components. The results obtained from GC-MS were found to be more discriminating than HPTLC. Excellent differentiation was achieved within pens from the models of same make. The major advantage of present study is the limited damage caused to the document. The methodology adopted in present study could be applied in the alteration cases in the suspected documents.

Keywords: Questioned document examination, high performance thin layer chromatography, gas chromatography-mass spectrometry, gel pen inks, volatile components.

Introduction

Gel pen is one of the most favoured writing instruments for writing and signing important documents such as will, agreements, medical bills and bank cheques. However, alteration made in such documents is a major concern for forensic document examiners. Alteration by different pens can be proved by matching the analytical profiles of suspected ink entries present on questioned document. Two inks are said to be different if they do not reveal any significant, reproducible, inexplicable difference at any level of optical and chemical analyses or *vice versa* [1]. Gel pen inks are mixture of dye or pigment based colourants and aqueous based solvents. Additional components include resins, lubricants, biocides, surfactants, corrosion inhibitors, sequestrants, sheer thinning agents, emulsifying agents, pH buffers and adjusters, polymerisation agents and pseudoplasticisers [2]. So far, significant improvements had been made in the analytical methods to analyse above described components. Nevertheless, there are still limited works published on the analysis of gel pen inks in comparison to ball point pen inks.

Separation technique like Thin Layer Chromatography (TLC) [3-5], High Performance Thin Layer Chromatography (HPTLC) [6-10] and high performance liquid chromatography [11] have been used to study the colour components of ink. TLC and HPTLC are inefficient methods to analyse pigment based gel pen inks but were suitable for the analysis of dye based gel pen inks. They have been utilised to analyse blue and black gel pen inks conducted in Romania, United States and India [6-10]. However, colour components constitute only minor portion of an ink formulation, and therefore information obtained was therefore limited. For additional information, an examiner has to rely on techniques that are easily available, causes less damage to document, high sensitive and of low cost. Gas Chromatography-Mass Spectrometry (GC-MS) fulfills all these requirements and has been used to classify the black gel pen inks manufactured in different countries [4, 5, 12]. Both HPTLC and GC-MS were investigated in this study for their potential to differentiate blue, black, red and green gel pen inks manufactured in India.

Materials and Methods

Sample collection and preparation

A total of 90 gel pen samples (blue, black, red and green colours) were acquired from local stationary shops of India. The collected pens were marked with unique sample IDs. Each pen was used to write the phrase "document examination" multiple times on A4 sheets. Each prepared sheet was placed in separate envelope and stored in closed cabinets at room temperature. Four discs (1 mm) of ink strokes were punched from each prepared sheet

using a metal hand held puncher. The discs were then dissolved in 60 µL of analytical grade ethanol (China). Blank paper dissolved in ethanol was taken as control.

High performance Thin Layer Chromatography method

The samples were analysed using HPTLC unit (Camag, Switzerland) equipped with sample applicator and TLC scanner. About 10 µL of prepared ink sample was spotted on pre-coated HPTLC silica gel plates (Merck, Germany) of 20 cm × 10 cm dimension aided by Camag Linomat IV spot applicator. The parameters, including sample volume, position of bands, band width, distance between relative bands and scanning range were controlled by Win Cat Software installed in a personal computer. The syringe was washed twice with ethanol: water (1:1) after each application to remove any existing traces of previous ink samples.

The spotted plates were then allowed to develop in two solvent systems, namely ethyl acetate: ethanol: distilled water (70:35:30) and n-butanol: ethanol: distilled water (50:10:15). The developing time for both the solvent systems was 25 minutes and 50 minutes, respectively. The developed plates were then visualised under white light and ultraviolet lights. The results were primarily interpreted on the basis of differences in hR_f value of the spots under day and ultraviolet lights. The undifferentiated samples of primary analysis were then examined at 535 nm, 587 nm, 628 and 631 nm, respectively.

Gas Chromatography-Mass Spectrometry method

GC-MS analysis was performed using Shimadzu GCMSQP2010 Ultra equipped interfaced with AOCi auto-injector. Column used for separation was Rtx5sil MS, 30 m × 0.25 mm × 0.25 µm film thickness (1,4-bis-(dimethylsiloxy) phenylene dimethyl polysiloxane). Helium gas at flow rate of 1.40 mL/min was used. 3 µL of prepared ink sample was injected into the injector port at 220°C. The oven programme was set at 40°C, held for 1 minute, 10°C/min to 220°C and held for 2 minutes, followed by 10°C/min to 300°C and held for 2 minutes. After separation, the individual components migrated into the MS through transfer line set at 280°C. The scanning was performed from 39-400 a.m.u. The results were obtained in the form of total ion chromatogram (TIC).

Results

High Performance Thin Layer Chromatography

HPTLC analysis was performed on 28 gel pens out of 90, which were soluble in ethanol: water (1:1). These inks considered as dye based gel pen inks and were analysed using HPTLC. The HPTLC profile of few ink samples found different from others on the basis of their number of bands, colours and hR_f. In case of blue gel pen inks, blue, violet and pink colour dyes dominated among all ink samples (Figure 1). The presence of pink and violet colour bands have been reported in blue gel pen inks of Indian origin [3]. In addition to these, few dark blue bands have also been observed. Only two ink samples (BG51 and BG52) showed fluorescence in UV illumination at the wavelength of 366 nm (Figure 2).

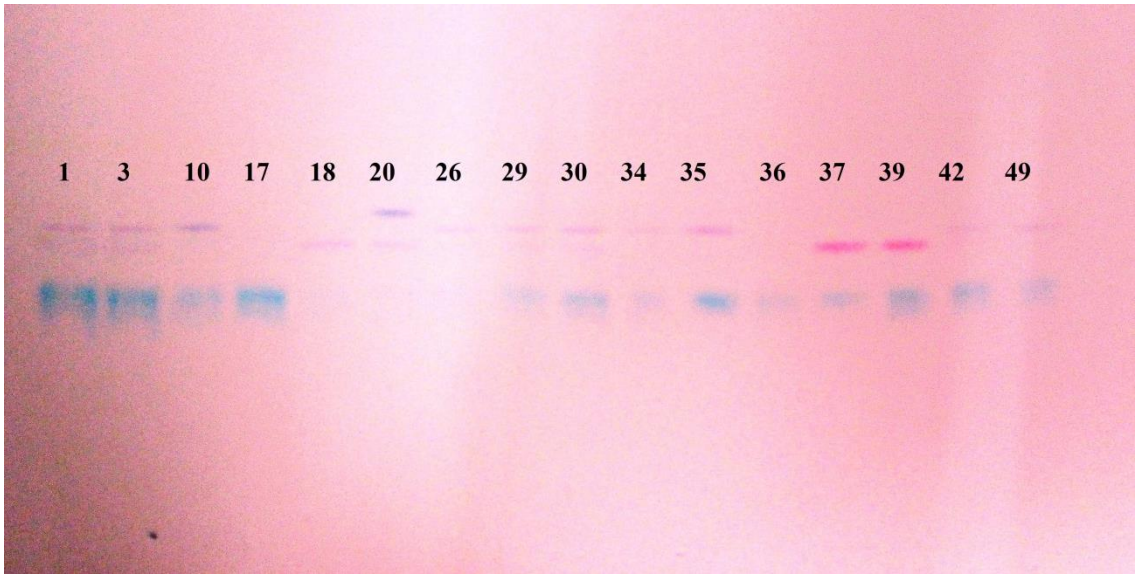

Figure 1: HPTLC chromatogram of blue gel pen inks in solvent system I under visible light

Samples that undifferentiated by primary analysis were then subjected to TLC scanner at 535 nm, 587 nm, 628 nm and 631 nm. For example, blue gel pen inks BG 1 and BG3 were similar in term of their band numbers, colours and hRf values in visible and ultraviolet illumination but able to be differentiated on the basis of additional spots detected at 628 nm (Table 1). No additional spots have been observed at other pre-set wavelengths. This led to the differentiation of blue gel pen inks into ten groups (Group 1-10), black gel pen inks into three groups (Group 1-3), red gel pen inks into one group (Group 1) and green gel pen ink in one group (Group 1). Similar results have been obtained for both solvent systems (solvent system I and solvent system II).

In this study, good differentiation was evident among pens from the models of same make. For example, black gel pen inks marked as BLG 13 (techno-tip) and BLG 14 (hydra-gel) which belonged to the same make, that is, flair but the HPTLC profiles of both ink samples were different from each other (Figure 2).

Table 1: Classification of gel pen inks into groups by HPTLC

Color of ink	Number of groups	Sample ID	Visible Light				Ultraviolet Light			Wavelength at 628 nm	
			Solvent system	No of Spots	Color of spots	hR_f	No of spots	Color of spots	hR_f	No of spots	hR_f
Blue	Group 1	BG1	I	2	Blue Violet	54 75	--------	--------	------	3	54,64,75
			II	2	Blue Violet	13 36	-------	-------	-------	3	13,26,36
	Group 2	BG 3	I	2	Blue Violet	52 74	--------	--------	--------	4	52,64,74,85
			II	2	Blue Violet	13 36	-------	-------	-------	4	13,26,36,48
	Group 3	BG 26	I	2	Blue Violet	53 74	1	Blue	74	--------	----------
			II	2	Blue Violet	15 36	1	Blue	36	-------	-------
		BG 34	I	2	Blue Violet	53 75	1	Blue	74	--------	--------
			II	2	Blue Violet	13 36	1	Blue	36	-------	-------
		BG 35	I	2	Blue Violet	51 74	1	Blue	74	--------	--------
			II	2	Blue Violet	15 36	1	Blue	36	-------	-------
	Group 4	BG 42	I	2	Blue Violet	52 74	--------	--------	--------	--------	--------
			II	2	Blue Violet	14 36	-------	-------	-------	-------	-------
		BG 49	I	2	Blue Violet	53 75	--------	--------	--------	--------	--------
			II	2	Blue Violet	13 36	-------	-------	-------	-------	-------
	Group 5	BG 51	I	2	Blue Violet	53 76	2	Green Orange	85 76	--------	--------
			II	2	Blue Violet	13 35	2	Green Orange	55 35	-------	-------
		BG 52	I	2	Blue Violet	54 75	2	Green Orange	85 76	-------	-------
			II	2	Blue Violet	13 35	2	Green Orange	55 35	-------	-------
	Group 6	BG 17	I	1	Blue	52	------	--------	------	3	52,62,64
			II	1	Blue	14	------	-------	------	3	14,26,36
	Group 7	BG 36	I	1	Blue	54	-----	--------	------	--------	--------
			II	1	Blue	13	------	-------	------	-------	-------
	Group 8	BG 18	I	2	Blue Pink	53 64	1	Orange	64	-------	-------
			II	2	Blue Pink	14 26	1	Orange	26	-------	-------
		BG 37	I	2	Blue Pink	54 64	1	Orange	64	--------	--------
			II	2	Blue Pink	14 24	1	Orange	24	-------	-------
		BG 39	I	2	Blue Pink	54 63	1	Orange	63	--------	--------
			II	2	Blue Pink	14 26	1	Orange	26	-------	
	Group 9	BG 10	I	2	Blue Red	24 39	2	Black Green	39 55	-------	-------
			II	2	Blue Red	24 28	2	Black Green	23 30	-------	-------

	Group 10	BG 20	I	3	Blue Pink Dark Blue	53 64 84	1	Orange	64	-------	-------
			II	3	Blue Pink Dark Blue	14 27 37	1	Orange	27	-------	-------
Black gel Pen inks	Group 1	BLG 2	I	--------	--------	------	-----	-----	-----	-----	-----
			II	--------	--------	-----	-----	-----	-----	-----	-----
		BLG 7	I	--------	--------	-----	-----	-----	-----	-----	-----
			II	--------	--------	-----	-----	-----	-----	-----	-----
	Group 2	BLG 10	I	2	Blue Red	24 39	2	Black Green	39 55	-------	-------
			II	2	Blue Red	24 28	2	Black Green	23 30	-------	-------
		BLG 14	I	2	Blue Red	24 39	2	Black Green	39 55	-------	-------
			II	2	Blue Red	24 28	2	Black Green	26 28	-------	-------
	Group 3	BLG 13	I	3	Blue Yellow Red	24 37 39	2	Black Green	39 55	-------	-------
			II	3	Blue Yellow Red	24 28 30	2	Black Green	24 29	-------	-------
Red gel pen inks	Group 1	RG1	I	1	Pink	37	1	Black	37	-------	-------
			II	1	Pink	29	1	Black	29	-------	-------
		RG 3	I	1	Pink	36	1	Black	37	--------	--------
			II	1	Pink	28	1	Black	29	-------	--------
		RG7	I	1	Pink	35	1	Black	37	-------	--------
			II	1	Pink	29	1	Black	29	-------	--------
		RG8	I	1	Pink	37	1	Black	37	-------	--------
			II	1	Pink	27	1	Black	29	-------	--------
Green gel pen inks	Group 1	GG4	I	2	Yellow Blue	24 28	2	Black Green	39 55	-------	-------
			II	2	Yellow Blue	24 26	2	Black Green	24 29	-------	-------

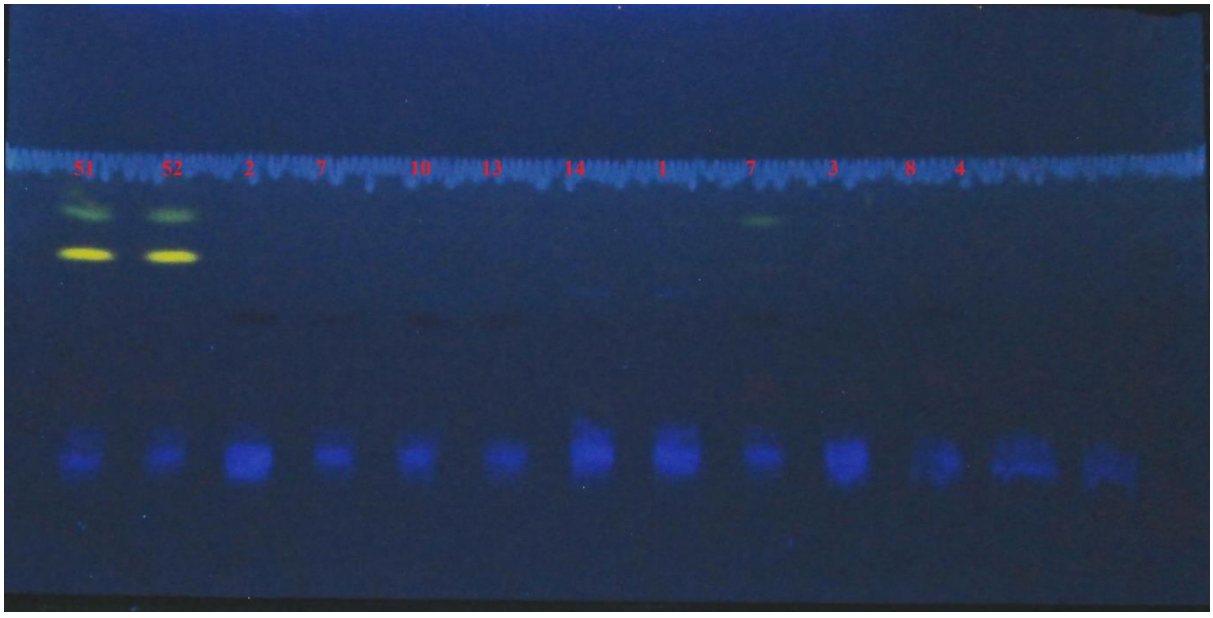

Figure 2: HPTLC chromatogram of blue gel inks (track 51 and 52), black gel inks (track 2,7,10,13 and 14), red gel inks (track 1,3,7 and 8) and green gel ink (track 4) in solvent system II under ultraviolet luminescence

Gas Chromatography-Mass Spectrometry

Interpretation of the GC-MS profiles of 90 ink samples were carried out primarily on the basis of major components. Samples which showed no major component were grouped in a miscellaneous group. Further differentiation depends on the specific component identified for each ink sample. Identification of components was performed through National Institute of Standard and Technology library search. Figure 3 illustrates the total ion chromatogram of black gel pen ink.

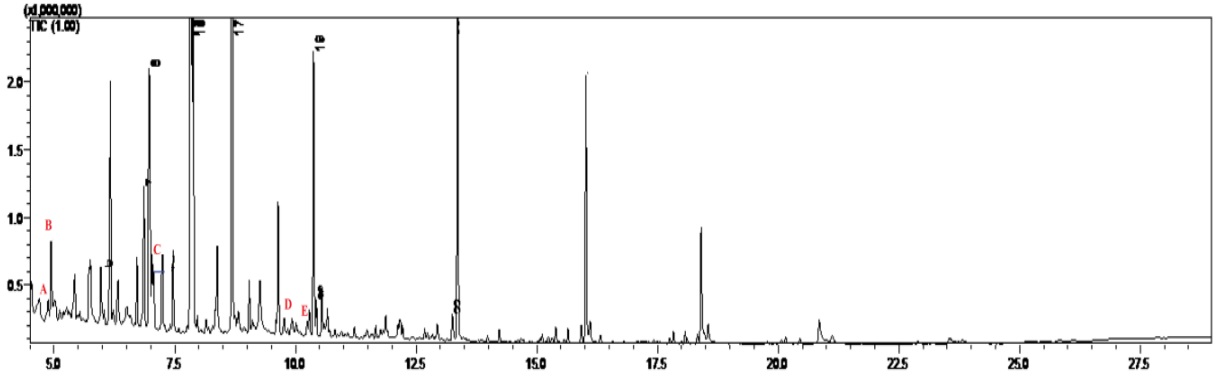

Figure 3: Total ion chromatogram of a blue gel pen ink representing (A) 2 trimethylsilyl methanol (B) ethylene glycol monoacetate (C) 2,2,6 trimethyl 3,5 heptadione (D) 1,2,4,5 tetramethyl benzene (E) 1,1 thio bis octane

Major components identified in black gel pen inks include 1,1-diethoxy-3-methylbutane; 4,4-dimethoxy-2-methyl-2-butanol and 2-methyl-1,3-dioxolane. The combinations of these major components distribute the entire black gel pen into three groups (Group 1-3) (Table 2). Group 1 consisted of ten samples which could be further differentiated based on specific components, *i.e.* vanillin, tert-butylmethylsilyl ether, 2-butanol, 3-methyl acetate, propanoic acid, phenol, cyclopropanetetradecanoic acid, 2-octyl-methyl ester, alpha-hydroproxy diethyl ether; 3-methyl-5-propyl nonane, bis-2,2'-[methylenebis(oxy)] propane, urethane and 2-deoxypentopyranose. Similar procedure carried on other pen ink samples successfully classified blue gel pen inks into six groups (Group 1-6), red gel pen inks into one group (Group 1) and green gel pen inks into one group (Group 1) (Table 3-5). This study allowed the differentiation of 85 out of 90 gel pen inks.

Table 2: Differentiation of black gel pen inks based on GC-MS profiles

Groups (Number of samples)	Major Components	Sample Id	Other components	Retention Time (minutes)
Group 1 (10)	Butane,1,1 diethoxy- 3 methyl 4,4 dimethoxy-2-methyl-2-butanol 1,3 dioxolane, 2 methyl	BL 3	Vanillin, tert-butylmethylsilyl ether	6.156
		BL 4	2-butanol, 3-methyl acetate	5.576
		BL 6	Propanoic acid	6.85
		BL 7	Phenol	6.674
		BL 9	Cyclopropanetetradecanoic acid, 2-octyl-methyl ester	6.873
		BL 10	Alpha-hydroproxy diethyl ether	6.915
		BL 11	Nonane, 3-methyl-5-propyl	16.002
		BL 12	Propane,2,2'-[methylenebis(oxy)] bis	6.67
		BL 13	Urethane	4.6
		BL 14	2-deoxypentopyranose	5.218
Group 2 (3)	Butane,1,1 diethoxy- 3 methyl 1,3 dioxolane, 2 methyl	BL 2	Diethoxymethyl acetate	4.765
		BL 5	Pentane,1-(-ethoxyethoxy)-	6.555
		BL 8	Glycerol triethyl ether	6.405
Group 3 (1)	4,4 dimethoxy-2-methyl -2-butanol	BL 16	4,4 dimethoxy-2-methyl -2-butanol	4.838
	Miscellaneous	BL 1	Propanedioic acid, diethyl ester	7.197
		BL 15	----------	----------
		BL 17	2,5-dimethoxy-4ethylamphetamine	4.641
		BL 18	3-buten-2-one,4-(dimethylamino)-4-ethoxy	8.674
		BL 19	Dimethylmalonic acid, monochloride, 2 octyl ester	9.624

Table 3: Differentiation of blue gel pen inks based on GC-MS profiles

Groups (Number of samples)	Major components	Sample Id	Other Components	Retention Time (minutes)
Group 1 (18)	Butane 1,1 diethoxy-3 methyl	BG 3	1,3 dioxolane, 2 methyl	5.285
		BG 5	Ethanol 1'1 oxybis-diacetate	5.464
		BG 6	1,2 Ethanediol, monoacetate	4.809
		BG 7	2 methyl butane-1,4 diol, 3-(1ethoxy ethoxy)	7.230
		BG 8	----------	----------
		BG 13	Methoxy, phenyl oxime	5.885
		BG 16	1,2 epoxy-3-(2'-ethoxy)ethoxypropane	5.16
		BG 23	----------	----------
		BG 27	beta-D-Mannofuranoside,1-thio-n-heptyl	4.773

		BG 28	2-octanone,1-nitro	5.695
		BG 37	3-(-2 methoxyethoxymethoxy)-2-methylpentan-1-ol	7.019
		BG 43	3 methylheptadecane	18.07
		BG 44	Octane,1'1 -thiobis-	10.24
		BG 50	----------	----------
		BG 51	1,3-Diethoxy-2-propanol	7.031
		BG 52	5-Formyl-6-methyl-4,5 dihydropyran	8.38
		BG 53	5H-1,4-Dioxepin, 2,3-dihydro-2,5 dimethyl	5.707
		BG 54	1,3 dioxan-4-ol,2,6-dimethyl-,acetate	5.74
Group 2 (1)	Pentane, 1 butoxy	BG 31	Pentane, 1 butoxy	6.641
Group 3 (1)	1-Butanol, 3 methyl acetate	BG 35	1-Butanol, 3 methyl acetate	5.301
Group 4 (15)	Butane 1,1 diethoxy-3 methyl Pentane, 1 butoxy	BG 17	1,3 diethoxy-2propanol	7.053
		BG 18	(1-propyloctyl) cyclohexane	18.552
		BG 20	Methoxy (n-pentyloxy) methylsilane	6.699
		BG 21	Ethene, 1'1'-[oxybis(2,1-ethanediyloxy)-bis	4.711
		BG 24	----------	----------
		BG 25	2,4-dimethyl-3-cyclohexene-1carbaldehyde	12.8
		BG 26	2-isobutoxyethylbutyrate	8.78
		BG 32	5-oxohexanethioic acid, S-t-butyl ester	8.18
		BG 33	Boronic acid, ethyl-,diethyl ester	6.365
		BG 39	3-(-2-methoxy-ethoxymethoxy)-2-methyl-penta-1-ol	6.97
		BG 41	2-methylbutyl butyrate	8.284
		BG 46	Ethyl 4-(ethyloxy)-2-oxolate-3-enoate	5.677
		BG 47	2,2,6-trimethyl-3,5 heptadione	7.042
		BG 48	Glycine, N-(N-acetylglycyl)-butyl ester	5.778
		BG 55	1,2,4,5-tetrazin-3-amine, 6-(3,5dimethyl-1-pyrazolyl)	8.375
Group 5 (2)	Butane 1,1 diethoxy-3 methyl 1-Butanol, 3 methyl acetate	BG 19	Valeric acid, 2 ethoxyethyl ester	9.648
		BG 45	3-Heptanol,2-4 dimethyl	5.818
Group 6 (3)	Butane 1,1 diethoxy-3 methyl Pentane, 1 butoxy 1-Butanol, 3 methyl acetate	BG 22	----------	----------
		BG 42	1,2 cyclopropanedicarboxylic acid,3,3 dimethyl	7.009
		BG 49	6 methylhepatne-1,6-diol	5.615
	Miscellaneous	BG 1	Ethanol,1,1'-oxybis,-diacetate	5.421
		BG 2	Propanal,3-ethoxy	4.972
		BG 4	4-heptanone,-3,3,5-D4	5.969
		BG 9	1-ethoxy-1-pentoxy-ethane	12.205
		BG 10	Tri (propylene glycol) propyl ether	6.43
		BG 11	Carbonic acid,3-pentylpropyl ester	14.609
		BG 12	1,3 diethoxy-2-propanol	7.022
		BG 14	2,2'-trimethylenebis-1,3-dioxolane	8.39
		BG 15	Dimethylmalonic acid, monochloride, 2 octyl ester	9.625
		BG 29	Silicic acid, diethyl bis (trimethylsilyl) ester	9.038
		BG 30	Undecane, 4-cyclohexyl	16.104
		BG 34	2-Butenoic acid, 4-(tetrahydro-2H-pyran-2-yloxy)-methyl ester	4.674
		BG 35	3-ethyl-3-heptanol	5.185
		BG 36	(2-(2-butoxyisopropoxy)-2 propanol	11.384
		BG 38	----------	----------
		BG 40	1,3- dioxolane, 2-(1-propenyl)	5.21

Table 4: Differentiation of red gel pen inks based on GC-MS profiles

Groups (Number of samples)	**Major Components**	**Sample Id**	**Other components**	**Retention Time (minutes)**
Group 1 (1)	Propane 1,1 diethoxy	RG 1	2 Butenal, 2-Ethenyl	4.53
		RG 3	2,2,6-trimethyl 3,5 heptanedione	7.035
		RG 5	2-ethyl-n-butyric acid ethyl ester	5.762
		RG 9	3-heptanol 2,4 dimethyl	5.696
		RG 10	Glycine, N-(N-acetylglycl)-butyl ester	5.755
	Miscellaneous	RG 2	1,1-dimethoxybut-2-ene	4.737
		RG 4	2 butenal, 2 ethenyl	4.58
		RG 6	Pseudo uridine penta-tms	16.314
		RG 7	2-methylbutyl butyrate	8.26
		RG 8	3-methylheptadecane	18.063

Table 5: Differentiation of green gel pen inks based on GC-MS profiles

Groups (Number of samples)	**Sample Id**	**Other components**	**Retention Time (minutes)**
Group 1 (6)	GG1	1,1 diethoxy 3-heptanone	4.845
	GG2	Octanoic acid, ethyl ester	10.282
	GG3	Undecane, 4 cyclohexyl	18.546
	GG4	--------	----------
	GG5	n-nonadecanol-1	15.919
	GG6	----------	---------

Discussion

The components identified in the present study were much greater than those reported previously, where this study focused on both the major and minor ink components to classify gel pen inks. A number of researchers studied on specific ink components to differentiate black gel pen inks with SPME-GC-MS, but the cost and selective analysis of SPME-GC-MS had limited its availability in all forensic science laboratories. Therefore, GC-MS is more common over SPME-GC-MS in handling routine case examples related to ink evidence.

Dye based gel pen inks undistinguishable by HPTLC were completely differentiated using GC-MS (Figure 4). More components, including the solvents, plasticisers, co-polymers and resin could be determined by GC-MS as compared to HPTLC that restricted to dyes only. Apart from that, GC-MS with its high sensitive and selective nature allowed the determination of minor components present in an unknown ink sample. The major advantage of the present study was the minimum damage applied onto the document where previous studies [4-6] utilised 10-20 ink strokes (1 mm) for the analysis of gel pen inks but only four strokes (1 mm) were adequate to provide the desired results. Also, in actual scenario, an examiner could not provide his/her opinion solely on the basis of single technique due to the potential error rate, and therefore, the combination of two different methods successfully differentiated most samples in this study.

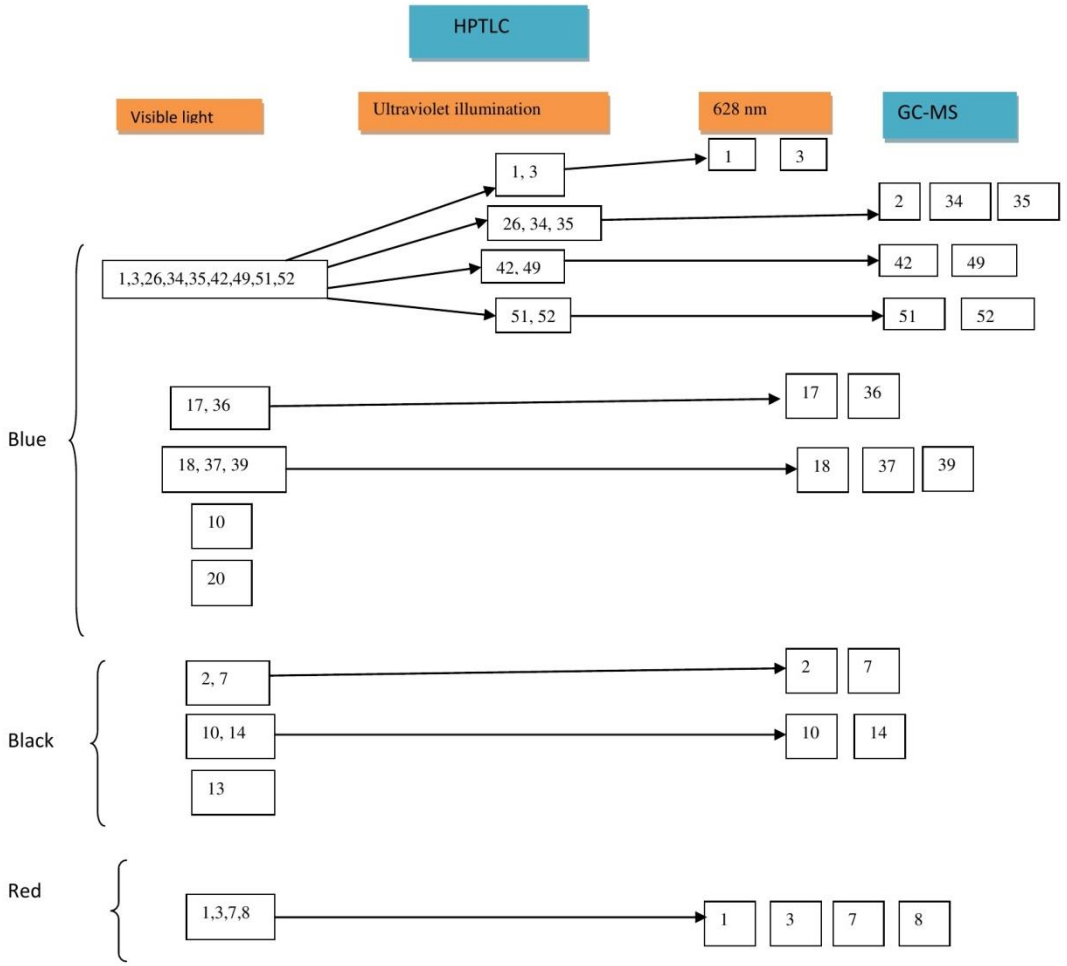

Figure 4: Schematic presentation of differentiation of gel pen inks using HPTLC and GC-MS

Conclusion

Both HPTLC and GC-MS proved to be effective, reliable and objective analytical tools to analyse gel pen inks. HPTLC was used to analyse dye based gel pen inks whereas GC-MS was used for the multiple omponents analysis. Maximum differentiation could be achieved based on the minor components rather than major ones. Therefore, minor peaks must take into consideration during data interpretation. Future studies could be suggested on the analysis of

different ink types, such as toners, inkjet inks and ball point pen inks using the proposed methods.

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