Using a MS library to differentiate black ballpoint pen inks by Py-GC/MS

[Background] Black ballpoint pens are one of the most widely used writing instruments; therefore the characterization of the ink is of interest to forensic chemists. Inks can often be differentiated based upon the their pyrograms. The pyrograms of 35 commercially available inks were used to create an “ink” library. An unknown ink was then analyzed and identified using the newly created library.

[Experimental] Each ink was scribed onto copy paper. A 5mm square of the marked paper was punched out and placed in a sample cup. 50 µL of dichloromethane was added to extract the ink components. The paper was subsequently removed and the solvent was evaporated using N_2. The sample was pyrolyzed at 550ºC. The integration-summation (INT-SUM) mass spectrum was calculated for each pyrogram. These were used to construct an “ink” MS library. One arbitrarily selected ink was used to test the viability of the library.

[Results] Pyrograms of the ”unknown” and four inks stored in the library are shown in Figure 1. The major components of each ink are solvents such as phenoxyethanol and dimethyl aniline. All elute before 7 min on the pyrogram. Inks A through D showed similar pyrograms; however, small peaks are observed after 7 min. These are dyes and additives and differ from ink to ink. It is difficult to differentiate the inks using only the INT-SUM* mass spectra (Fig. 2(a)), because of the presence of ions m/z 77, 94, and 138 which are from the phenoxyethanol. Thus, a second INT-SUM mass spectra was created from components eluting after 7 min on the pyrogram (Fig. 2 (b)). Now, significant differences in match quality are observed and the “unknown” ink can easily be identified as Ink C. One way to differentiate samples with similar major components is to exclude the common components when constructing the library.

(*JP Pat: 3615480)

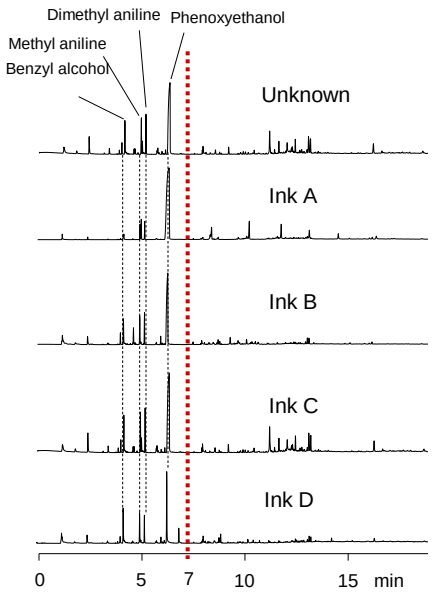
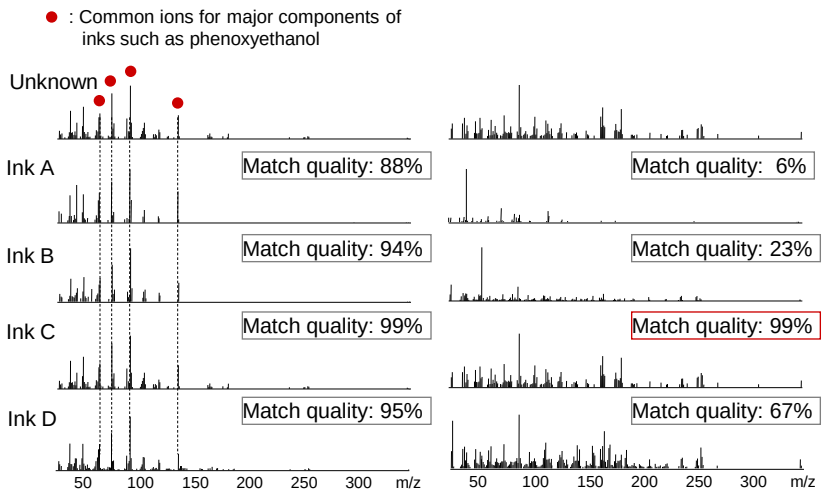


Fig. 1 Pyrograms of oil-based black ballpoint pen inks

Pyrolysis temp.: 550ºC, GC oven: 40 - 300ºC (20ºC/min)
Separation column: Ultra ALLOY⁺-5 (5% diphenyl 95% dimethylpolysiloxane, L=30 m, i.d.=0.25 mm, df=0.25 µm), Carrier gas: 1 mL/min, He
Split ratio: 1/50, sample: ca. 200 µg



(a) Mass spectra created from entire pyrogram (0-20 min)

(b) Mass spectra created from pyrograms of components eluting after 7 min.

Fig. 2 Comparison of mass spectra created (a) from entire pyrogram and (b) from components eluting after 7 min.

Ref: Watanabe et al., 8th annual meeting of Japan Association of Forensic Science and Technology (2002)

Keywords : Oil-based black ballpoint ink, Water soluble, non soluble black ink, Forensic discrimination, MS library

Products used : Multi-functional pyrolyzer, Vent-free GC/MS adapter, F-Search

Applications : Identification, Forensic investigation, Printing

Related technical notes : PYA3-013E

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