

CASE REPORT

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Mass Spectrometry in Forensic Chemistry: 1. Pigment Identification by Direct Mixture Analysis in a Case of Bank Note Falsification

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ABSTRACT: A rapid mass spectrometry procedure, based on direct mixture analysis using conventional electron ionization in both the low and high resolution modes, was used to match pigments present on a counterfeit \$100 United States bank note with pigments contained in two inks suspected of having been used. The results demonstrated that the pigments present on the false bank note and those contained in the inks were the same.

KEYWORDS: questioned documents, mass spectrometry, inks, pigments, counterfeit currency, direct mixture analysis, bank note falsification

Mixture analysis by mass spectrometry (MS) generally requires chromatographic separation of the components before ionization. Alternatively, it can be performed by collision activation tandem mass spectrometry (MS/MS) without prior separation. In some circumstances, however, by exploiting the different volatilities of the mixture components, one can analyze the mixture, at least partially, by fractional volatilization in the ion source by way of a direct-insertion probe. In this paper, the authors describe a rapid mass spectrometry procedure, based on this simple, direct mixture analysis, which was used to identify the pigments present on a counterfeit bank note (United States \$100) by comparing them with two inks suspected of having been used to produce the bank note.

Case Report

During inquiries into the circulation of counterfeit bank notes, the police received a counterfeit United States \$100 bank note from an anonymous informer and the address

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where it might have been printed. An authorized search revealed a light filter and two green inks used in offset printing. The examining magistrate ordered an expert examination to determine whether the bank note was counterfeit and, if so, whether the light filter and the two green inks had been used to produce it. The bank note was a poor counterfeit; the green circle on the right of the recto side with the number 100 overprinted in black was fully out of register and coincided completely with the light filter. A chemical analysis was performed to ascertain whether the pigments present in the green circle matched those contained in the two green inks.

Materials and Methods

Materials

Standard pigments copper, (^{29}H , ^{11}H -phthalocyaninate(2-)- ^{29}N , ^{30}N , ^{31}N , ^{32}N) or Blue 15 (C.I. 74160) [1] and butamide,2,2'-((3,3'-dichloro(1,1'-biphenyl)-4,4'-diyl)bis(azo))bis(N-(2,4-dimethylphenyl)-3-oxo) or Yellow 13 (C.I. 21100) [2] (Fig. 1), both of which were present in the two inks, were obtained from one of the ink manufacturers. The solvents were C. Erba (Milan, Italy) reagent-grade products.

Methods

The portion of the bank note out of register and two pieces of paper previously treated separately with the two inks were extracted with chloroform (CHCl_3) in an ultrasonic bath for 2 h. An AEI (Kratos, Manchester, United Kingdom) MS30 double-focusing mass spectrometer was used in conjunction with a Kratos DS-55S data system. Low- and high-resolution electron ionization mass spectra were recorded at 70 eV energy ionization and 3 kV acceleration potential. The standard pigments, a mixture of the standard pigments, and the extracts were loaded onto the direct-insertion probe tip, and the probe temperature was gradually increased up to 330°C. This procedure resulted in the fractional distillation of the mixture components in the ion source, as has been described for mixtures of peptides [3-4].

Results and Discussion

The mass spectrum in the 250 to 700 mass unit range of the pigment Yellow 13, recorded at 260°C, is shown in Fig. 2. The molecular ion is at m/z 684, and the fragmentation pattern is consistent with the molecular structure. The isotopic distribution of the molecular ion demonstrates the presence in the molecule of two chlorine atoms ($^{35}\text{Cl}/^{37}\text{Cl}$, 75/25). High-resolution mass measurement of the molecular ion gave a value of 684.2028. This is in good agreement (with an error of approximately 1.5 ppm) with the exact mass value 684.201 842, corresponding to the elemental composition ($\text{C}_{16}\text{H}_{14}\text{O}_4\text{N}_6\text{Cl}_2$) of pigment Yellow 13. To our knowledge, this is the first time that an electron impact mass spectrum of pigment Yellow 13 has been reported.

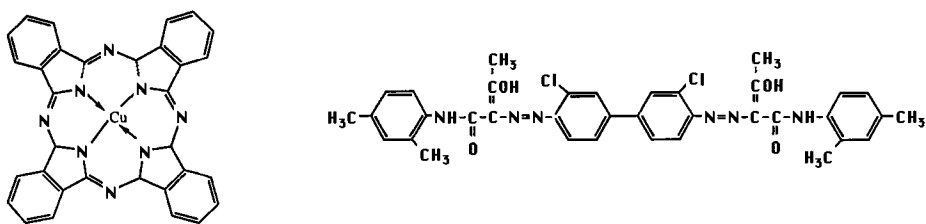


FIG. 1—Molecular formulas of pigment Blue 15 (left) and pigment Yellow 13 (right).

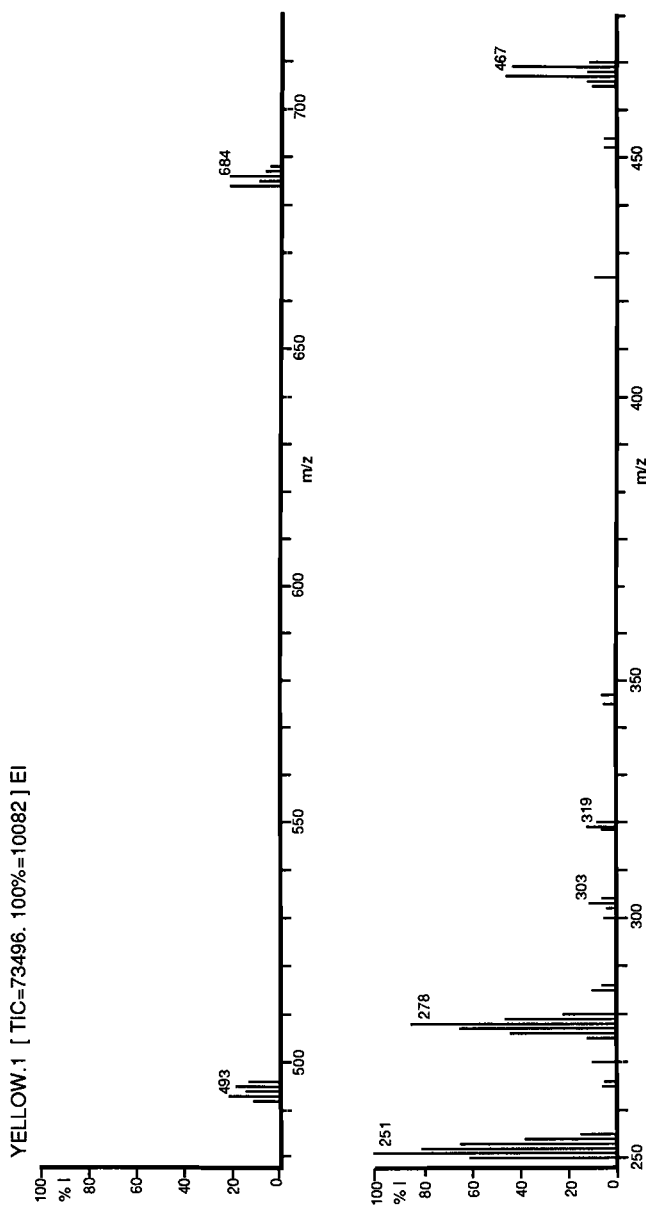


FIG. 2.—Electron ionization mass spectrum of the pigment Yellow 13 in the range 250 to 700 mass units, recorded at 260°C.

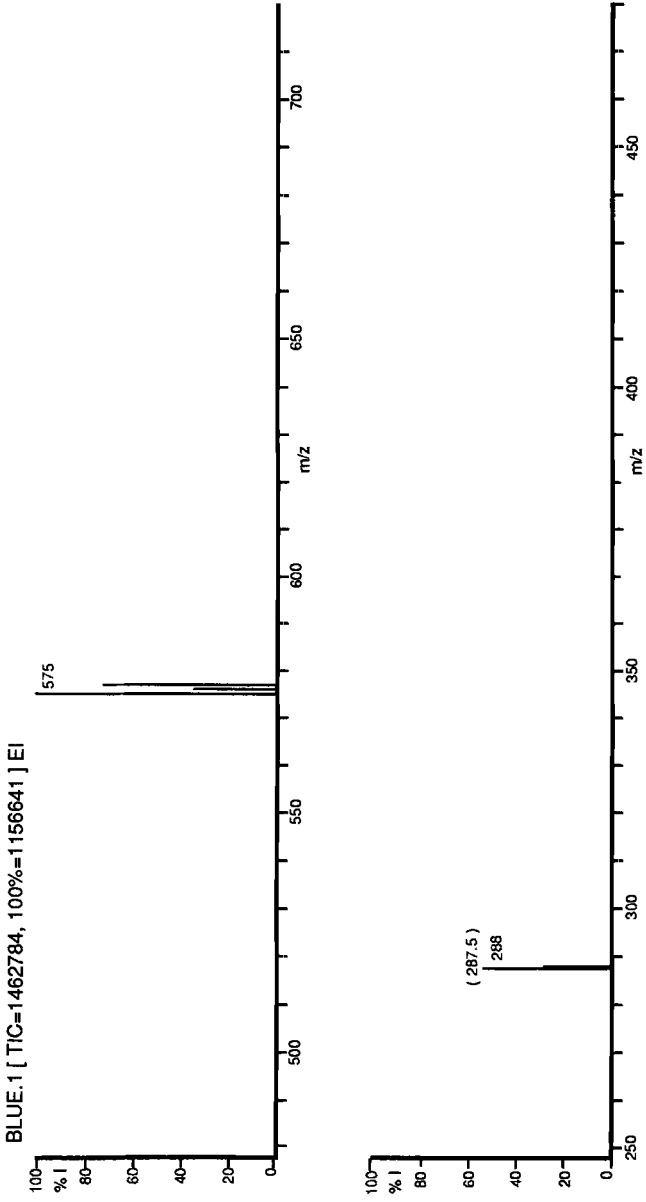


FIG. 3—Electron ionization mass spectrum of the pigment Blue 15 in the range 250 to 700 mass units, recorded at 310°C.

The mass spectrum of the pigment Blue 15 (Fig. 3), recorded at 310°C, revealed only single and double charged molecular ions at m/z 575 and 287.5, respectively, because the highly conjugated and coordinated structure of the molecule prevents fragmentation. The isotopic distribution of the molecular ion showed one copper atom ($^{63}\text{Cu}/^{65}\text{Cu}$, 69/31) in the molecule. The exact mass observed for the molecular ion was 575.0802, which is in good agreement (with an error of approximately 1.5 ppm) with the mass value of 575.079 383, corresponding to the elemental composition ($\text{C}_{32}\text{H}_{16}\text{N}_8\text{Cu}$) of pigment Blue 15. Electron ionization mass spectra of phthalocyanines have been reported elsewhere [5].

Because the above mass spectra were recorded at very high temperatures and a temperature difference of 50°C, the two pigments in the mixture could be analyzed, both on the counterfeit bank note and in the two inks, even though other components with low and medium boiling points were present. In fact, below 250°C, all the contaminants were evaporated. In the ranges 250 to 270°C and 300 to 320°C, the mass spectra of pigments Yellow 13 and Blue 15, respectively, showed a high degree of purity. Finally, in the range 270 to 300°C, the mass spectrum corresponded to the sum of the mass spectra of the pigments and to the chloroform extract of the counterfeit bank note (Fig. 4). The background produced by other compounds in the mixture could have been subtracted, but this did not hamper identification of the pigments because the background did not exceed m/z 320.

Figures 5 and 6 show the mass spectra recorded at 260 and 310°C, respectively, of the bank note extract. We compared these mass spectra with those of the standard pigments Yellow 13 and Blue 15 (Figs. 2 and 3) and measured the exact mass values for both the peaks at m/z 684 and 575. The averages of the masses were 684.2032 and 575.0805; these values are in good agreement (with an error of approximately 2 ppm) with the exact molecular weights of pigments Yellow 13 and Blue 15, respectively.

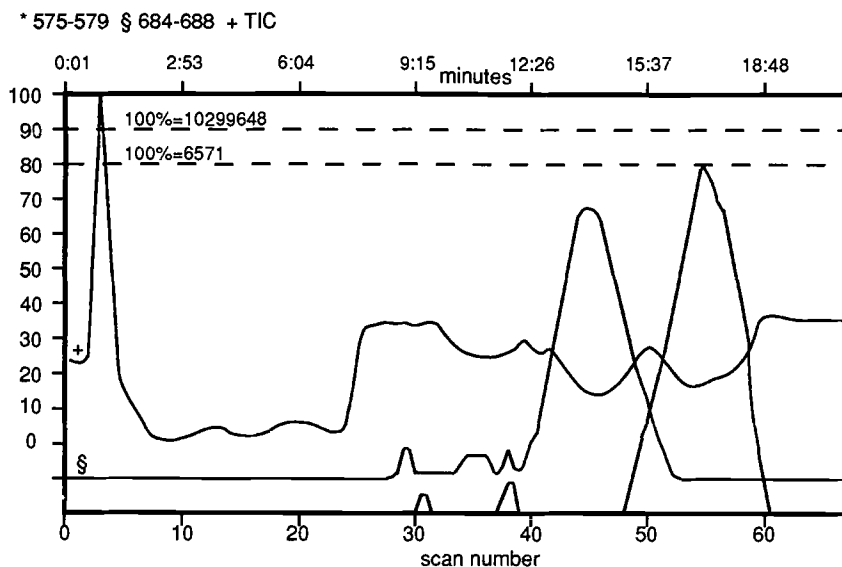


FIG. 4—Total ion chromatogram and ion chromatograms of the Yellow 13 and Blue 15 molecular ion regions obtained from the analysis of the chloroform extract of the counterfeit bank note.

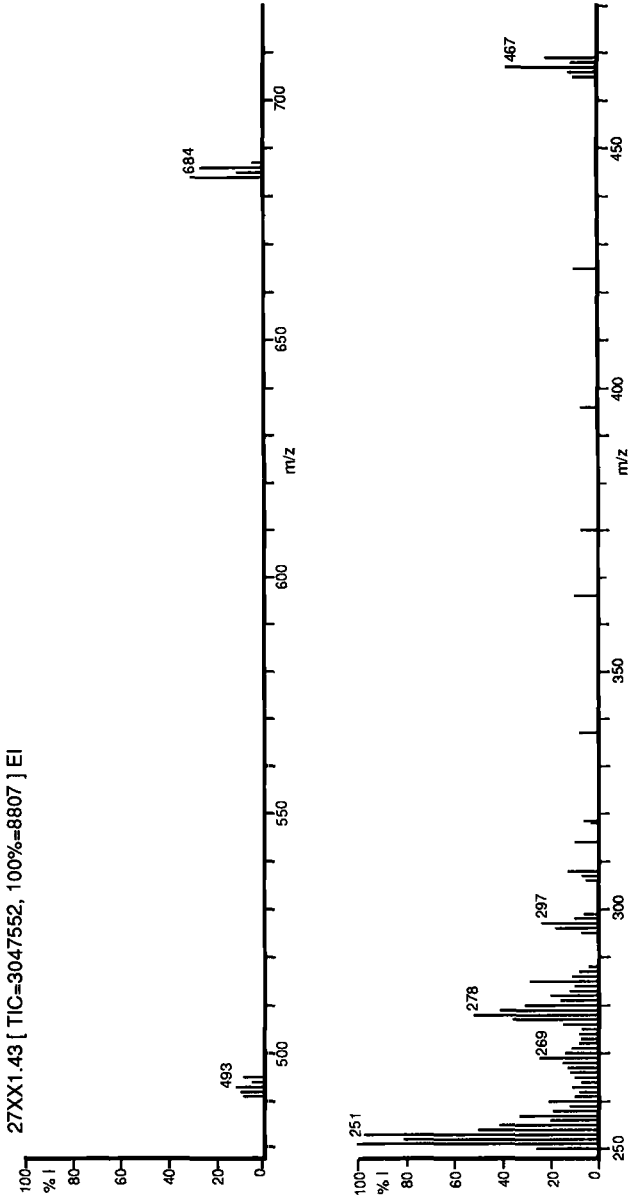


FIG. 5.—Electron ionization mass spectrum of the counterfeit bank note extract recorded at 260°C.

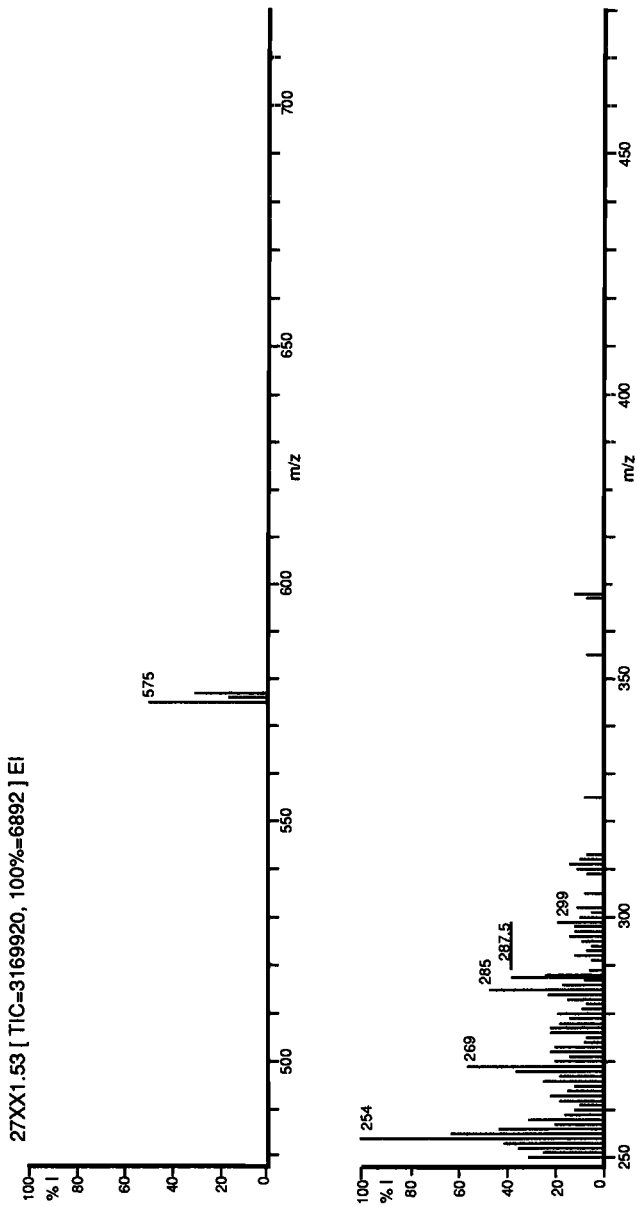


FIG. 6—Electron ionization mass spectrum of the counterfeit bank note extract recorded at 310°C.

Conclusions

These findings demonstrate that the pigments present on the counterfeit bank note are the same as those used to produce the inks examined. This represents only circumstantial evidence, since these pigments are present in various inks made worldwide, and it would be practically impossible to prove conclusively that a particular ink was used to produce the counterfeit bank note. Nevertheless, in this case, on the basis of spectrometric results and with the match between the counterfeit bank note and the light filter, the printer was committed for trial.

In conclusion, mass spectrometry, without previous chromatographic separation of the components, is a useful, rapid method with which to analyze such mixtures.

References

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