

Characterization of historical writing inks by different analytical techniques

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Characterization of eight historical writing ink samples was performed using different analytical techniques. UV, visible spectroscopy, thin layer chromatography and capillary electrophoresis were used for the analysis of ink aqueous solutions. Characterization by UV and visible spectroscopies and capillary electrophoresis revealed specific features in historical inks fabricated under different recipes, providing a possibility to determine the identity of historical inks regarding their chemical composition. However, there is a clear indication that the chromatographic technique used for the characterization of historical writing ink samples was unsuccessful. The evaluation of the results obtained from thin layer chromatography does not offer the possibility to identify effectively the nature of various ingredients in different ink samples.

Key words: historical writing inks, UV spectroscopy, visible spectroscopy, chromatography, capillary electrophoresis, qualitative analysis

INTRODUCTION

Important historical documents, manuscripts, maps in libraries and archives suffer very serious damage as a result of the destructive effects of different kind of inks. The reasons for this destruction are not yet fully understood [1-4]. Hundreds of recipes for ink have been published over centuries [5, 6]. The great variety of ink recipes and the variety of visual aspects of manuscripts suggest that many side effects could occur and contribute to the different aspects of paper degradation.

Several analytical techniques such as proton-induced X-ray emission spectroscopy, gas chromatography coupled with mass spectrometry, atomic absorption spectrometry, reflectance spectrometry, scanning electron microscopy, energy dispersive X-ray microanalysis, X-ray photoelectron spectroscopy and IR spectroscopy have been applied for determining the constituents of ink [7-14]. Most of these techniques are complex and generally require several time-consuming analytical steps. Besides, some methods are based on very expensive instrumentation. In this paper, we report the application of UV-visible spectroscopic, thin layer chromatographic and capillary electrophoretic techniques for the characterization of different historical writing ink samples, such as Pfalz ink from red wine, ink from oak bark extract, different iron gall inks, black ink with iron (II) sulphate,

black ink with copper sulphate and logwood tree ink. Our study is oriented to the determination of the specific features of different inks depending on their chemical composition.

EXPERIMENTAL

Eight different writing ink samples were prepared using the following recipes [14]. Analytical grade reagents and distilled water were used for the preparation of inks.

Recipe 1. *Pfalz ink from red wine*; 100 ml of red wine (Bulgaria) was carefully mixed with 5 g of powdered cherry gum (ZAO, Sankt-Peterburg) and 4 g of soot (Kremer Pigmente). The obtained mixture was stored for 2 weeks in a closed vessel with intermediate (daily) shaking. The pH of the final ink solution was equal 3.51.

Recipe 2. *Ink from oak bark extracts*; the bark of oak (61 g; Švenėionys Herbs, Lithuania) was mixed with 610 ml of distilled water and left for three days. The obtained mixture was slowly boiled for 4 h, allowed to cool and filtered. To this solution, 30 ml of red wine (Bulgaria) was added. After mixing, the volume of the obtained solution was reduced up to 50 ml by slow evaporation. The pH of the final ink solution was 3.69.

Recipe 3. *Iron-gall ink*; ~16 ml of cold distilled water and ~1 ml of 10% acetic acid (Lachema) were added to powdered oak galls (1 g; Kremer Pigmente), iron (II) sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) (0.53 g; Flu-

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ka)) and gum arabic (0.53 g; Kremer Pigmente). After a careful grinding the mixture was stored for 8 weeks with intermediate mixing in a slightly covered vessel and filtered. The pH of the final ink solution was 1.66.

Recipe 4. Black ink with iron (II) sulphate; 66.8 ml of distilled water was mixed with 7.688 g of powdered oak galls and the mixture was stored for 3 days. To this, 2.528 g of iron (II) sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), 0.2 g of sodium chloride (NaCl; Aldrich), 2 ml of 10% acetic acid and 0.318 g of alum ($\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$; Aldrich) were added. The obtained mixture was stored for 2 weeks with intermediate mixing and filtered. The pH of the final ink solution was 1.52.

Recipe 5. Black ink with copper (II) sulphate; 66.8 ml of distilled water was mixed with 7.688 g of powdered oak galls and mixture was stored for 4 days. To this, 2.528 g of copper (II) sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$; Fluka), 0.2 g of sodium chloride (NaCl), 2 ml of 10% acetic acid and 0.318 g of alum ($\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) were added. The obtained mixture was stored for 2 weeks with intermediate mixing and filtered. The pH of the final ink solution was 2.14.

Recipe 6. Logwood tree ink; 100 ml of distilled water, 20 g of logwood tree (Kremer Pigmente), 1.5 g of gum arabicum and 0.1 g of chromium alum ($\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$; Aldrich) were carefully mixed. The obtained mixture was filtered. The pH of the final ink solution was 5.73.

Recipe 7. German recipe A; 50 ml of distilled water, 4 g of gallic acid ($(\text{HO})_3\text{C}_6\text{H}_2\text{COOH}$; Aldrich), 1.0 g of gum arabicum and 1.0 g of iron (II) sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) were carefully mixed. The obtained mixture was filtered. The pH of the final ink solution was 1.94.

Recipe 8. German recipe B; 100 ml of distilled water, 0.7 ml of 10% hydrochloric acid (HCl; (Lachema)), 0.77 g of gallic acid ($(\text{HO})_3\text{C}_6\text{H}_2\text{COOH}$), 1.0 g of gum arabicum, 2.34 g of tannin (Kremer Pigmente), 0.1 g of phenol ($\text{C}_6\text{H}_5\text{OH}$; Aldrich) and 3.0 g of iron (II) sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) were carefully mixed. The obtained mixture was filtered. The pH of the final ink solution was 1.62.

The prepared different ink samples were characterized by UV and visible spectroscopies using a Perkin-Elmer FTIR Spectrum Lambda 20 and SF-26 spectrophotometers, respectively. Capillary electrophoretic analysis was performed on a P/ACE 2100 apparatus (Beckman Instruments) equipped with a UV detector with wavelength filters (200, 214, 230 and 254 nm). Fused silica capillary (Polymicro Technology, Phoenix, AZ, USA) of 75 μm I.D. and 57 cm total length (50 cm to the detector) was used. The samples were introduced in the hydrodynamic mode by overpressure ($3.43 \cdot 10^3$ Pa). Thin-layer chromatograms (TCL) were performed on Cavalier UV 254 silufol plates. The composition of the sam-

ples was checked by TCL using an eluent of alcohol (methanol, ethanol, isopropanol) and water at different ratios. The chromatograms were dried in the air and treated with dithizone solution in carbon tetrachloride. A Mettler-Toledo MP220 pH meter was employed for measuring pH values of inks in the aqueous phase.

RESULTS AND DISCUSSION

The UV spectra of all ink samples are presented in Fig. 1. According to the origin of the absorptions, it

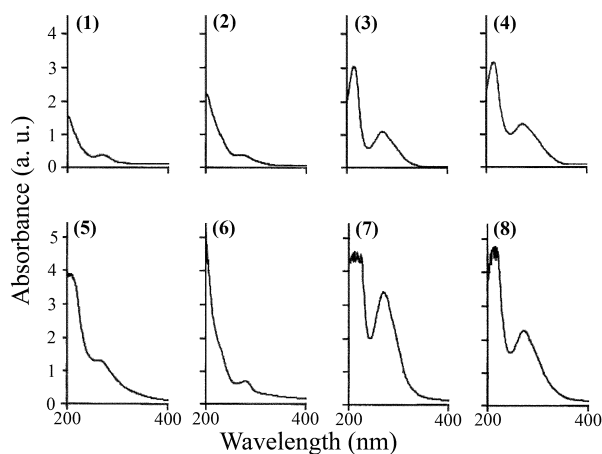


Fig. 1. UV spectra of ink samples prepared according to recipes 1–8

is clearly seen that the study inks differ in their chemical composition. For instance, the UV spectra of the Pfalz ink from red wine (recipe 1), ink from oak bark extracts (recipe 2) and Logwood tree ink (recipe 6) contain only weak absorption bands at 275, 281, and 283 nm respectively. It is interesting to note that the UV spectra originating from inks 1, 2 and 6 showed no significant differences. This is not surprising, since ink from the oak's bark extracts contains the same red wine as the sample prepared according to recipe 1. Also, the chemical composition of oak bark is expected to be very similar to that of cherry gum or Logwood tree.

The distinctive features observed in the UV spectra of iron gall inks prepared with powdered oak galls (recipe 3 and 4) are two intensive absorption bands at 215 nm (sharp) and 269 nm (broad). More intensive absorptions at the same wavelengths are observed in the UV spectra of iron gall inks prepared with gallic acid instead of natural products from the powdered oak galls (recipe 7 and 8). These absorptions are typical absorptions of Fe^{2+} complex with gallic acid (see Fig. 2). As is seen from Fig. 2, the absorptions of Fe^{2+} – gallic acid complex are slightly shifted to shorter wavelengths region in comparison with the bands (218 and 274 nm) in the UV spectrum for pure gallic acid. A slight similarity between

UV spectra of iron gall inks and the spectrum of copper gall ink prepared with powdered oak galls (recipe 5) could be identified. However, the most intensive absorption band is even more shifted to the higher energies (210 nm). The distinctive feature of the spectrum obtained from copper gall ink is the low intensity and broad character of the second absorption (275 nm) as compared with absorptions from iron gall inks. Moreover, this weak shoulder is not very well pronounced.

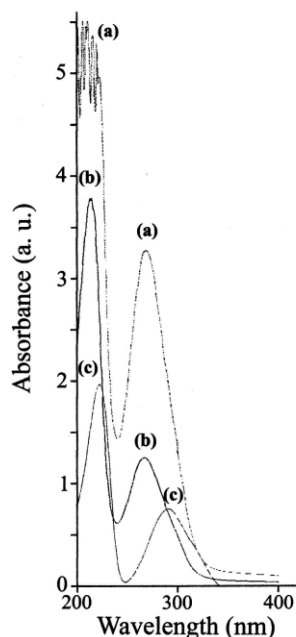


Fig. 2. UV spectra recorded for different Fe^{2+} mixtures with gallic acid (a and b) and gallic acid (c) at concentrations of FeSO_4 0.025 mol/l (a) and 0.01 mol/l (b); and gallic acid 0.0125 mol/l (a and c) and 0.005 mol/l (b)

UV spectroscopic evaluation of different ink samples provides a possibility to identify historical inks regarding their chemical composition. According to the specific features in the UV spectra, the investigated inks can be roughly classified into four categories: (a) iron gall inks containing as ingredients iron sulphate and powdered oak galls, (b) iron gall inks containing iron sulphate and gallic acid, (c) copper gall inks containing copper sulphate and powdered oak galls, and (d) inks in which colours originate through natural dyes. However, such classification of the spectra is fairly speculative. For instance, the UV spectra of iron and copper gall inks prepared using natural products from oak galls show insufficient difference.

In Fig. 3, optical spectra in the visible region over the range of 400–750 nm for aqueous solutions of the same ink samples are compared. The variation of intensities of absorption bands between 400 and 750 nm was found to be very similar (from 0.5 to 1.5) for each ink sample. Therefore, Fig. 3 represents only a qualitative comparison of the electronic

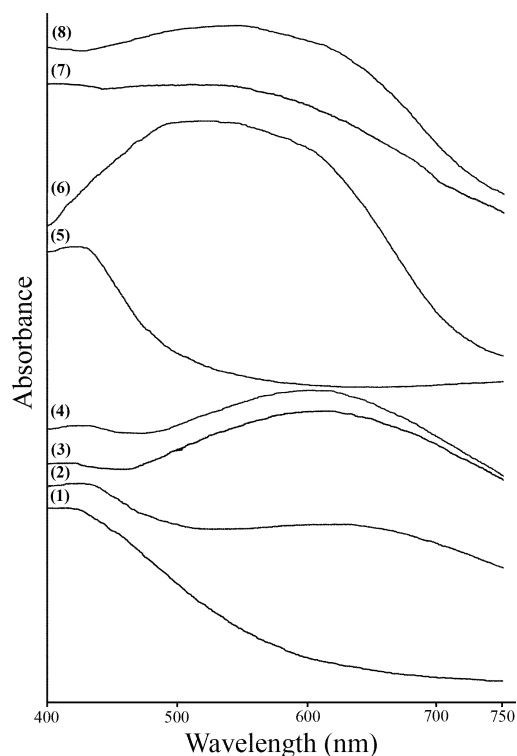


Fig. 3. Electronic spectra of ink samples prepared according to recipes 1–8

spectra for several historical writing inks. Interestingly, the spectra of the iron gall ink samples (recipes 3, 4, 7, and 8) were nearly the same, irrespective of their chemical composition. These spectra show only one very broad absorption band with $\lambda_{\text{max}} \approx 590\text{--}610$ nm, which is in good agreement with literature data [10]. However, it is evident that the visible spectrum of copper gall ink sample (recipe 5) could be easily distinguished from those of iron gall inks. The spectrum of copper gall ink contains a shoulder at $\lambda_{\text{max}} \approx 400\text{--}425$ nm, and contrary to the iron gall inks does not show any absorption in the 590–610 nm region of wavelengths. The similar electronic spectra could be observed for the Pfalz ink (recipe 1) and ink from oak bark extracts (recipe 2). On the contrary, the Logwood tree ink (recipe 6) shows a characteristic electronic spectrum with a well pronounced λ_{max} at ≈ 500 nm. From these measurements it is evident that visible spectroscopy could be effectively used for the qualitative analysis and direct characterization of aqueous solutions of gall inks containing different metals [5, 6, 15]. The characteristic absorptions from the specific constituents are also very significant and could be used for the qualitative determination of the identity of inks.

All ink samples were examined by thin-layer chromatography using silufol plates. The schematic view of the obtained chromatograms was almost the same for different ink samples. All inks having a different chemical composition after drying with dithizone were detected as light brown spots with $R_f = 0.72\text{--}0.74$

on a yellow background. Thus, we can conclude from chromatographic measurements that these methodological approaches could not be successfully used for the analysis and direct characterization of aqueous solutions of historical inks.

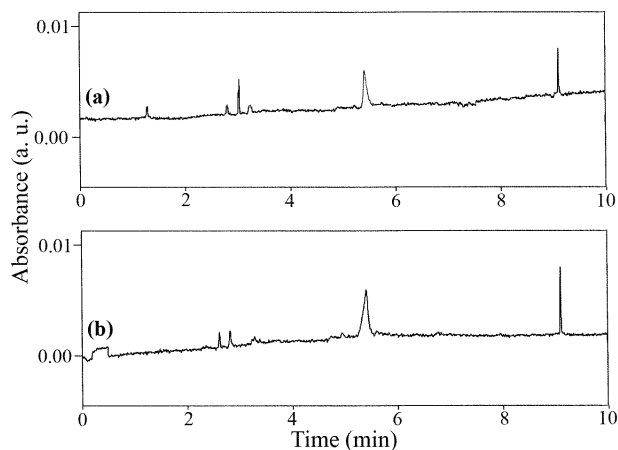


Fig. 4. Electropherograms of ink samples prepared according to recipes 1 (a) and 2 (b). Electrolyte, 0.025 mol/l Tris-phosphate, pH 8.0; hydrodynamic injection for 10 s; voltage, 25 kV; direct UV detection at 254 nm

In addition, the capillary electrophoretic method was applied for the analysis of aqueous solutions of all historical ink samples. Figure 4 shows two electropherograms of inks which colours originate from the natural dyes (recipes 1 and 2). The both electropherograms are almost identical with two main peaks at ~5.42 min and ~9.11 min and several less intensive peaks in the range of 2.6–3.5 min. The electropherograms of the second group of inks (recipes 3, 4, and 5) containing iron or copper sulphates and natural products from oak galls as ingredients were almost identical. Figure 5 shows a representative electropherogram for ink sample prepared according to the recipe 5. A sufficient difference from previous ones (Fig. 4), however, could be easily detected. As

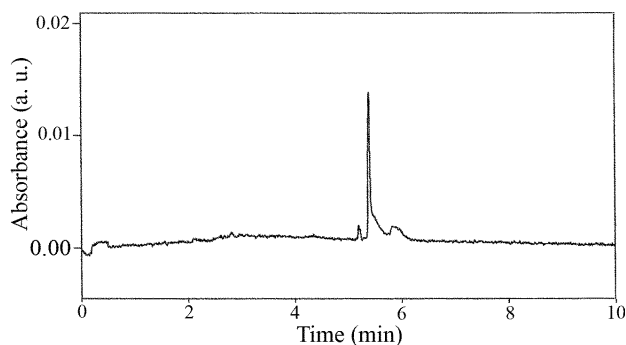


Fig. 5. Electropherogram of ink sample prepared according to recipe 5. Electrolyte, 0.025 mol/l Tris-phosphate, pH 8.0; hydrodynamic injection for 10 s; voltage, 25 kV; direct UV detection at 254 nm

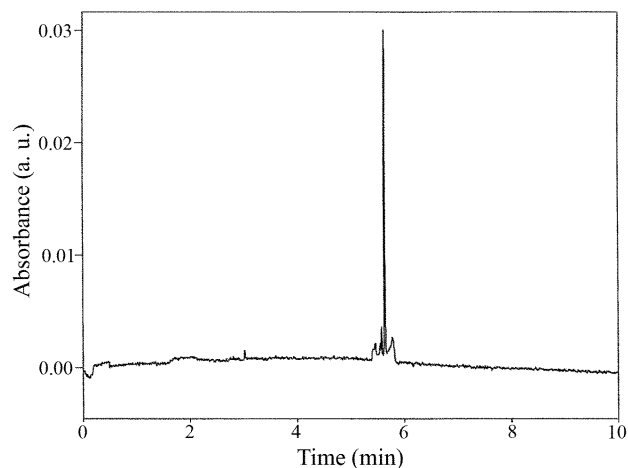


Fig. 6. Electropherogram of ink sample prepared according to recipe 6. Electrolyte, 0.025 mol/l Tris-phosphate, pH 8.0; hydrodynamic injection for 10 s; voltage, 25 kV; direct UV detection at 254 nm

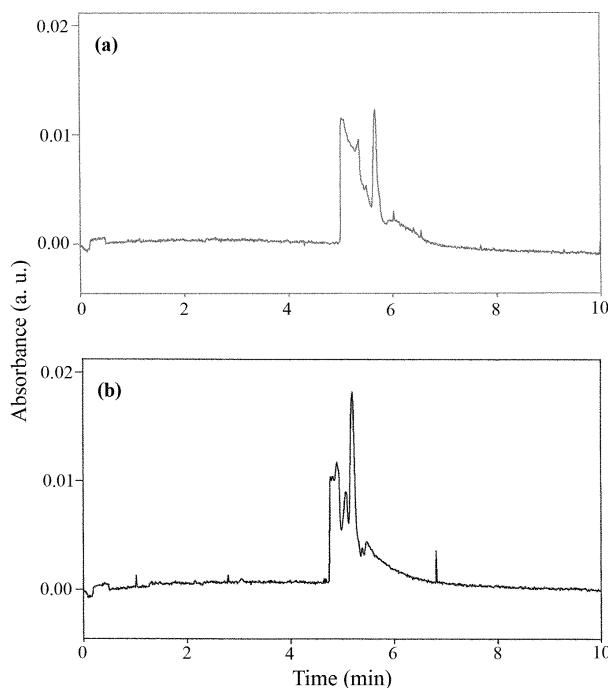


Fig. 7. Electropherograms of ink samples prepared according to recipes 7 (a) and 8 (b). Electrolyte, 0.025 mol/l Tris-phosphate, pH 8.0; hydrodynamic injection for 10 s; voltage, 25 kV; direct UV detection at 254 nm

is seen from Fig. 5, the electropherogram contains one very intensive peak together with alongside located two less intensive satellites. The well-resolved peak around 5.5 min for the ink samples prepared according to the recipes 3, 4 and 5, possibly could be attributed to the mesence of metal gallate complexes [16–18] in the composition of inks. The electropherogram of ink sample prepared according to the recipe 6 (Fig. 6) contains a very well resolved characteristic peak at ~5.7 min and several other pe-

aks with a sufficient separation selectivity. The electropherograms of iron gall inks prepared using gallic and tannic acids (recipes 7 and 8) are shown in Fig 7. Apparently, these two electropherograms differ from those containing natural products from oak galls, having the characteristic features in the range of 4.6–5.9 min. Thus, we can conclude that historical inks could be easily identified by the capillary electrophoretic technique [19]. On the whole, it appears that the capillary electrophoretic method is a suitable and promising technique not only for the approximate qualitative analysis but also for a rapid quantitative investigation of historical inks [20].

CONCLUSIONS

In this investigation, eight different historical writing inks have been investigated and characterized by different analytical techniques: UV and visible spectroscopy, thin layer chromatography and capillary electrophoresis. It was clearly shown that UV-visible spectroscopic and electrophoretic evaluation of different ink samples provides a possibility to identify historical inks regarding their chemical composition. According to the observed specific features, the inks were classified into several categories: (a) inks whose colours originate from natural dyes; (b) iron (copper)-gall inks prepared using natural products from oak galls; (c) metal sulphate inks additionally containing natural dyes; (d) iron-gall inks prepared using gallic and tannic acids. According to our results, the thin layer chromatographic analysis of ink aqueous solutions, however, could not be used for the direct characterization of historical ink samples. On the other hand, to our knowledge, a successful use of capillary electrophoresis for analyzing the composition of fingerprints of different ink samples has not been previously reported. In summary, the results demonstrate that UV-visible spectroscopy and capillary electrophoresis may provide very important information on the chemical composition of historical writing inks which could be useful for the investigation of various degradation mechanisms of inks and for elaboration of new the methods of conservation of historical paper documents.

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ISTORINIŲ RAŠALŲ APIBŪDINIMAS AVAIRIAIS ANALIZINIAIS METODAIS

Santrauka

UV bei regimosios spektroskopijos, plonasluoksnės chromatografijos ir kapiliarinės elektroforezės metodai buvo taikyti avairiems istoriniams rašalams apibūdinti. Pirmą kartą parodyta, kad UV bei regimosios spektroskopijos, taip pat kapiliarinės elektroforezės metodai sėkmingai gali būti pritaikyti avairių sudėčių istoriniams rašalams identifikuoti. Be to, iš pateiktų rezultatų akivaizdžiai matyti, kad kapiliarinės elektroforezės metodas gali būti išplėtotas ir istorinių rašalų sudedamųjų dalių kiekybinėje analizėje. Taip pat nustatyta, kad plonasluoksnės chromatografijos metodo taikymas efektyviam istorinių rašalų identifikavimui yra problemiškas. Straipsnyje pateikti tyrimo duomenys leidžia padaryti išvadą, kad UV bei regimosios spektroskopijos, taip pat kapiliarinės elektroforezės metodais gauti rezultatai gali būti sėkmingai panaudoti tyrinėjant senovinių rašalų irimo mechanizmus bei kuriant naujas rašytinių dokumentų konservavimo technologijas.