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Ink Dating by the Examination of Solvent of Ball Point Ink by UV-Vis Spectroscopy

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Abstract

Background: When we talk about the age of documents, finding the age of ink on that document is the better option. Previously, many researches took place on various kind of inks and how to identify the age of that ink. It is called ink dating. Through this research we wanted to find out if we can perform ink dating with ultraviolet-visible spectroscopy as it is cheaper than any other instrumentation techniques and all the current techniques are not enough to accurately predict the age of the documents, they can only approximately predict the age of the document. Most have many limitations and most of the technique are destructive in nature. We need more research and development to find a technique which can reduce error rate as well as cost. Current technique can only measure the age to wide range like 1000 years old-10 years old but these technique fails if we try to find the age of document of 5 or less year old.

Result: In this research, we collected sample of ink of different age, written on same kind of paper with same ink brand. The pens are manufactured at same batch of ink. Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (FTIR-ATR) was performed on the sample to identify the component of the ink to find the maximum absorption of these components. The ink samples of different aged ink were examined through UV-Visible spectroscopy after the ink isolation by Solvent extraction method and when the samples were examined through UV-Vis Spectrophotometer, no direct relation was found between the results *i.e.*, the readings of the spectrophotometer were random at two different wavelengths 500 nm and 600 nm.

Conclusion: After this experiment, we can conclude that it is not possible to estimate the age of the ink using only UV-Visible spectrophotometer.

Keywords: Ink dating • FTIR-ATR • UV-Vis spectroscopy • Solvent extraction method

Abbreviations: UV: Ultraviolet; Vis: Visible; IR: Infrared; TLC: Thin Layer Chromatography; GC: Gas Chromatography; FTIR-ATR: Fourier Transform Infrared Spectroscopy-Attenuated Total Reflectance

Introduction

Writing ink is the most common technique to document the information on a paper. It is used from ancient times, previously the writing instrument were brushes, sticks, bamboo etc. Modern writing instruments like pen have specialized inks [1]. These writing inks are made up of colorant, solvent, stabilizer and additives. Inks are of two types, oil-based and water-based. Oil-based inks include ballpoint pen inks, whereas water-based includes pilot pen inks, fountain pen inks etc. The colorant in oil-based pens are pigments and in water-based pens, it is dyes. Solvents are usually alcohols; these are also called vehicles. Stabilizers are used to prevent the ink from clotting and make the ink smoother to flow. Other additives are used to improve other quality of the ink [2].

Writing ink have colorant, the visible component of any ink. Colorant in ink can be of two types; pigment and dyes. Pigments are present in glycerol-based inks, whereas dyes are present in water-based ink. Pigments are usually finely grounded colored particles suspended in solvent. These pigments form a thin layer on the surface of the paper while writing. Dyes stain the paper material and make the writing visible. Dyes are tended to fade faster than pigments. Solvents are the vehicle of an ink; all the components of an ink are suspended in it. The solvent should be volatile in nature, so that after writing it should vaporize leaving the colorant on the paper. That's why the solvents are alcoholic in nature e.g., acetone, propyl

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alcohol, propylene glycol etc. Ballpoint pen have oil-based solvents and fountain pen have water-based solvents. Stabilizers are used to give the ink better flow. It gets attached to the molecules of the ink and prevent them to adhere with each other [3]. This makes the ink smooth in texture too. These are basically the polymers of large molecules. In the ancient times, plant resin and egg albumin were used as stabilizers in the ink. Other additives include chemicals which maintain the pH of the ink, because if the pH of the ink is not maintained it can destroy the paper as well as the pen. Petroleum products to lubricate the ink. Ink tags, specific to the manufacturer to identify the ink. Many researches were conducted to find the age of the ink but it's still not accurate and contain error [4].

In this paper, we collected documents of different ages written with same brand of Ink on a same type of paper and we performed comparative study using the instrument UV-Vis spectrophotometer and we also performed FTIR-ATR on the ink sample to know the component of the ink.

Materials and Methods

The first step of ink extraction is to identify the type of ink e.g., if it is an oil-based ink or water based or any other ink. As water-based inks are soluble in water but other type of inks or oil-based inks need strong organic solvents to dissolve. We can use traditional method of extraction, *i.e.,* moist the cotton or gauge with respective solvent and gently rub the cotton on the ink, the ink will be transferred to the cotton. The other technique of ink extraction can be cutting the part of the paper into small pieces (1 cm^2) and performing solvent extraction technique. We can also use syringe needle and plunger to punch out the ink from the document and then place it in a test tube and put few drops of solvent and dissolve the ink in the solvent. Advance techniques include TLC and GC [5].

For isolation of Ink from the documents, we selected traditional method of ink isolation *i.e.,* solvent extraction.

Selection of solvent for ink extraction

Common solvents in ball point pen includes alcohols, polyhydric alcohols and glycol monoethers. That also means Inks are readily soluble in these.

- Examples of the alcohols includes ethanol, propanols, butanols, iso-butyl alcohol, tert-butyl alcohol, pentanols, benzyl alcohol and other various higher alcohols.
- Examples of the polyhydric alcohols include glycols having 2 or more carbons and 2 or more hydroxyl groups within the molecule, Such as ethylene glycol, diethylene glycol, etc.
- Examples of the glycol monoethers include ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monopropyl ether, etc. Also, glycol monoesters can be used similarly to the glycol monoethers [6].

The solvent we selected for isolation of Ink is Isopropyl alcohol for blue and black ball point ink and red ball point ink was readily soluble in pyridine. Red ball point ink was not soluble in isopropyl alcohol.

Isolation of ballpoint pen ink (blue and black)

We collected some documents of different dates ranging from 2019 to 2022 and used traditional method of ink isolation *i.e.*, we cut the document into 1 cm^2 pieces and placed those pieces in the glass beaker and poured isopropyl alcohol in it (3 ml each). After sometime, we noticed that the ink started to separate from the document. We removed the paper pieces and the ink was isolated in the alcohol. We tried different brands and different aged inks [7]. The method is working in all the inks. Instead of TLC, we will use this method as the method is quick and cheap. Later, we collected some documents of different dates ranging from 8/2019, 9/2019, 10/2019, 11/2019, 01/2020, 02/2020 and 03/2020. The pen brand used for these documents is cello fast-O ball point pen. We used traditional method of ink isolation *i.e.*, we cut the document into 1 cm^2 pieces and placed those pieces in the glass beaker and poured Isopropyl alcohol in it (3 ml each) as shown in Figure 1. After sometime, we noticed that the ink started to separate from the document as shown in Figure 2. We removed the paper pieces and the ink was isolated in the alcohol. We tried same brands of different aged inks [8]. The change in intensity of the color of the ink can be seen. We collected black ink sample from 11/2019 and tried this method and isolated the ink successfully but this method is not working for red ballpoint pen ink. Aniline gives partial isolation of red ink. Red ball point ink was successfully isolated by pyridine.

Figure 1. Glass beaker and poured isopropyl alcohol in it (3 ml each).

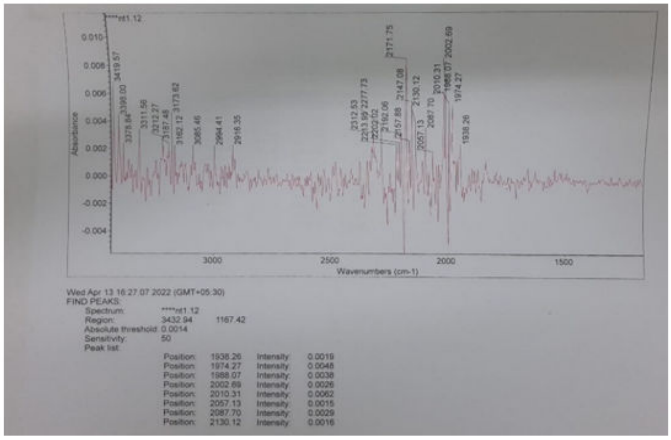

Figure 2. Ink started to separate from the document.

FTIR-ATR

For the identification of the component of the ink, FTIR-ATR was performed on one of the samples. FTIR-ATR is a non-destructive technique used to identify the component of the chemical without any error. The technique is very sensitive and the results are taken with extreme care. The results of the FTIR are shown below in Figures 3 and 4.

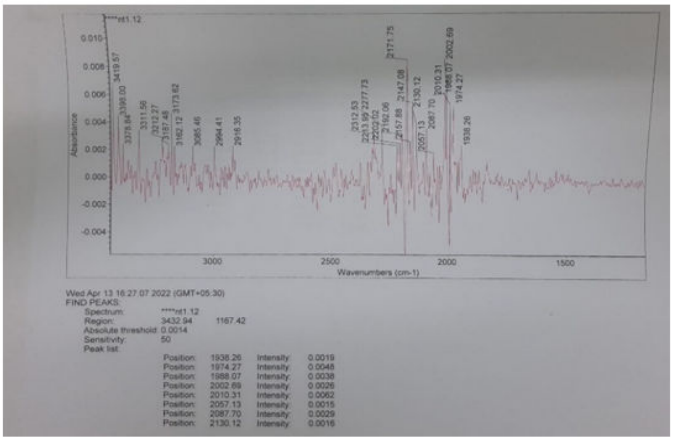

Figure 3. The results of the FTIR.

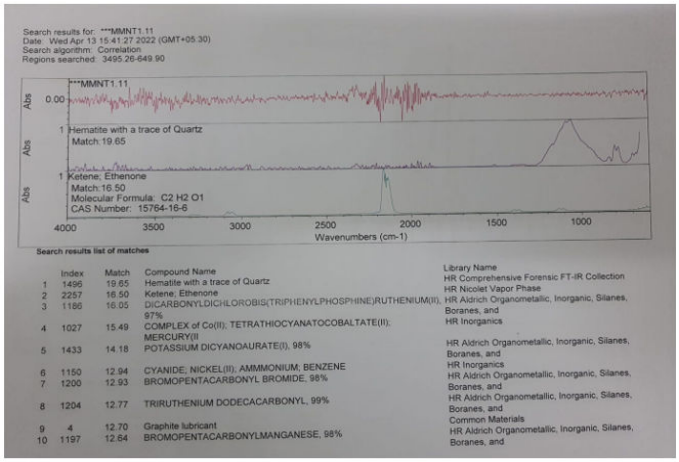

Figure 4. The results of the FTIR.

UV-Visible spectrophotometer

After the isolation of ink, the sample were placed in UV-Visible spectrophotometer at 500 nm and 600 nm wavelength and the absorption reading were noted with the samples, blank and the reference. The reference was the ink of same brand written freshly on the same type of paper [9]. To avoid the difference in the ink tags, the reference pen was manufactured on the same time with other pens. The blank contains isopropyl alcohol without ink.

Results and Discussion

In court of law, many cases involved disputed documents. These cases can be solved if we can calculate the age of the documents. When it comes to identifying the age of the document, the best method is to identify the age of the ink. Age of ink or ink dating can be calculated by various technique. Earlier in 1968, for ink dating, the identification of the composition of ink and to compare it from the standards in the ink library was done. The ink composition can be determined by TLC. Later on in 1975, with the modification of writing inks, the ink manufacturers started to add specific tags in the ink which can be identified for ink dating. Recently, the relative age comparison test or relative ink dating is done with the ink which have same formulation, same writing time or date and on the same type of paper or document. For relative ink dating, researcher developed many new methods and instrumentations. Method like solvent extraction (Rate determining procedure), it is premise that the longer the time ink had been placed on the paper, the more difficult it will be to dissolve in the solvent. But this method is not highly reliable and the chances of error is more. The second method is Fourier Transfer Infrared Spectroscopy (FTIR), as the solvent of the ink is volatile in nature and have alcohol group in its component and with time it can show variation. Many age versus several ratio of IR peak absorbance was observed. But this topic needs more experiment and result to produce more accurate results. Recent research by Cantu and Prough, they discovered a new technique for ink dating, it is called Extraction Rates by fluorescence analysis and they discovered the fluorescence component of the ink solvent and its relative optimum rate determining parameter of the different aged ink. They measured the fluorescent by fluorescence spectrophotometer. But the limitation of this method is that there should be no interference from the paper and also the solvent used for the extraction of the ink should not have any fluorescence components. For the ink with no fluorescence component, this method is not that much useful.

The first step of ink dating is the extraction of the ink and then after extraction the solvent can be analyzed. For analysis purpose, from previous researches we got to know that one can use gas chromatography especially for the detection of volatile component of the ink. We can also use Fourier Transfer Infrared (FTIR) spectroscopy for the detection of different component.

Relative age determinations have been reported using FTIR to detect changes in dried ink with age. In this work the Hydroxyl (OH) and

Methyl (CH) Infrared (IR) absorption bands were used. Humecki found a decrease in the ratio of the hydroxyl to methyl bands in 1 ink formulation up to 22 years old with the leveling off beginning around 10 years. Humecki used micro FTIR techniques since he was working with micro samples of ink (1 to 5 ram). Becker, et al., at ATF attempted to verify the usefulness of this technique using micro samples of ink; however, they did not use an IR microscope attachment as used by Humecki. Their results have been unsuccessful so far, perhaps because the optimum experimental procedures were not attained. However, the general trend of aging-versus-several ratios of IR absorbance peaks was observed. In all these cases, the ink extract is placed on a KBr window, although ATF also tried mixing KBr and making a pellet. It appears that the success of this technique depends on the extreme care that must be taken in sample preparation and on the use of an IR microscope. The setting of the apertures and placement of the sample in the microscope is critical [10].

The results of FTIR-ATR showed the presence of orange dyes and also other components.

The dye component found in the ink are:

- Hematite with a trace of Quartz
- Dicarbonyldichlorobis (triphenulphosphine)ruthenium(II)
- Potassium dicyanoaurate(I)
- Bromopentacarbonyl bromide
- Triruthenium dodecacarbonyl
- Bromopentacarbonylmanganese

After observing these components, the maximum absorption of these components is between 500 nm-600 nm. But the result we got is different from what we had expected. The path length of the spectrophotometer was 1 cm.

The result of UV-Visible spectroscopy is shown in Table 1.

Table 1. The result of UV-visible spectroscopy is shown in table.

Date of the document (Age)	Absorption reading at 500 nm	Absorption reading at 600 nm
0-Month-old ink (Reference) (April 2022)	0.231	1.055
32-Month-old ink (August 2019)	0.168	0.596
31-Month-old ink (September 2019)	0.287	1.356
30-Month-old ink (October 2019)	0.199	0.861
29-Month-old ink (November 2019)	0.368	0.777
28-Month-old ink (December 2019)	0.366	0.429
27-Month-old ink (January 2020)	0.404	0.435
26-Month-old ink (February 2020)	0.401	0.611
25-Month-old ink (March 2020)	0.258	1.204
Blank	0	0

Note: The blank showed no error in the reading.

Conclusion

Ink dating is a technique which helps us to approximately identify the age of the ink as well as the age of the documents. Every technique has some limitation when it comes to ink dating. In this research, we tried to use the application of UV-Visible spectroscopy in ink dating [11].

For that, we first used FTIR-ATR for the identification of the ink components and then carefully selected the wavelength at which those components show maximum absorption. The isolation of the ink from the document was done by solvent extraction method *i.e.*, cutting the document into 1 cm^2 pieces and placed those pieces in the test tube and poured Isopropyl Alcohol in it (3 ml each). After sometime, we noticed that the ink started to separate from the document. We removed the paper pieces and the ink was isolated in the alcohol. Then the samples were examined through UV-Vis spectrophotometer, no direct relation was found between the results *i.e.*, the readings of the spectrophotometer were random at two different wavelengths 500 nm and 600 nm. So, after this experiment, we can conclude that it is not possible to estimate the age of the ink using only UV-Visible spectrophotometer. Combining this technique with advance instruments may show variation in the results. But according to the results obtained in this experiment, we cannot conclude the age of the document or the ink.

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Declaration

I hereby declare that the article with the title "Ink dating by the examination of solvent of ball point ink by Uv-vis spectroscopy" submitted is the original work done by me in the guidance and supervision of Dr. Manisha Mann at Amity institute of forensic sciences, Amity University, Noida, Uttar Pradesh.

The work done in the report is genuine and has not been submitted previously for any other Journal.

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