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Analysis of Indian blue ballpoint pen inks tagged with rare-earth thenoyltrifluoroacetonates by inductively coupled plasma–mass spectrometry and instrumental neutron activation analysis

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Abstract

Characterization and assessment of inks on sensitive documents for absolute/relative age determination is the challenging forensic problem in spite of practical difficulties. Tagging of ballpoint pen ink with suitable taggant(s) is a unique method to come out with definitive inferences on the detection of forgery in documents written with ballpoint pens. Selection of a proper taggant primarily depends on sensitivity of analytical determination and their absence in normal varieties of ink used for document writing. Rare-earth elements, from all technical considerations can be potential taggant(s) for inks. To ensure more compatibility with ink, 13 rare-earth thenoyltrifluoroacetonate chelates were prepared and characterized. The ballpoint pen inks were tagged with rare-earth thenoyltrifluoroacetonate chelates individually at about 1–100 ppm level depending on sensitivity of element under suitable optimized experimental conditions and instrumental sensitivity. Aliquots of such tagged ink having varying amounts of taggants were analyzed by ICP–MS and INAA. Satisfactory recoveries and a good linear relationship of intensity (signal) against concentrations/amounts were observed. Under the optimized experimental conditions, the detection limits were worked out. This study of tagging metal ions in combination with ICP–MS and NAA as an analytical tool can allow to draw various combination options based on different rare-earth chelates as suitable materials for tagging of ballpoint pen inks for absolute/relative age determination to aid in document related crime examination. The advantages and limitations of proposed analytical techniques are discussed.

Keywords: Questioned documents; Inductively coupled plasma–mass spectrometry (ICP–MS); Instrumental neutron activation analysis (INAA); Blue ballpoint pen ink; Forensic science; Tagging; Rare-earth thenoyltrifluoroacetonates; Rare-earth elements (REEs)

1. Introduction

The analysis of ink with respect to both organic and inorganic components at trace and ultra-trace levels, is very important and valuable particularly in the examination of questioned documents including suspected addition of written text, forgery and counterfeiting where minimum amounts of sample are available for examination. This study is related to generation of characteristic pattern with respect to ink of definite origin which can help document examiners/ink chemists for detection of alteration or additions to a document and to determine the time when the document was written.

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The techniques employed for the analysis of inks can be divided into destructive and non-destructive methods. Non-destructive methods such as visible and infrared luminescence [1–3], diffuse reflectance infrared [4], fourier transform infrared spectroscopy [5,6] and microspectrophotometry [7,8], are valuable for document examination. For examination of ink with respect to the separation of organic components of ink, destructive methods such as thin layer chromatography (TLC) [9–11,17] and high performance thin layer chromatography (HPTLC) [12,13] have replaced the older technique of paper chromatography. Due to various advantages high performance liquid chromatography (HPLC) [14–16] has been used as an alternate destructive technique for separation of ink components. Gas chromatography (GC) (for volatile component) [17] and capillary electrophoresis (CE) [18–21] have also been used.

The tagging of ink with suitable organic or inorganic constituents is a useful method for the characterization of ink. If the ink contains a unique organic/inorganic taggant different from the other components present in normal varieties of ink, it can serve as a unique identification index. Moreover, if the inks are suitably tagged, it must be possible to obtain an idea about the nature and the year of manufacture of ink and help in detection of forgery and also judge the time of writing the documents. This procedure can be used for detecting cases of tampering of evidences subsequently. The work on tagging of ink by inorganic taggant followed by analytical determination employing X-ray excited optical fluorescence (XREOF) spectroscopy has been reported [22,23]. However, to our best knowledge only a few reports on tagging of ink are appeared in journals. In a feature article on Analytical Methods for Detecting Fraudulent Documents, Cantu [24] has illustrated the potential use of analytical methods for document dating in forensic science. Recently non-destructive techniques like EDXRF [25] and PIXE [21,26] have been used for determination of inorganic components of ink. Ink manufacturers do not disclose completely the ink composition for proprietary reasons. This research is aimed to generate data on possible tagging of ink and to prepare a database of information on the ballpoint pen inks available in India.

Among the various advanced and sophisticated analytical techniques, inductively coupled plasma–mass spectrometry (ICP–MS) and neutron activation analysis (NAA) are the most popular and widely used analytical techniques for simultaneous multi-element analysis at trace levels in diverse matrices. In inductively coupled plasma–mass spectrometry, a plasma is formed by noble gas (Ar), which is then utilized to ionize the elements in the sample matrix. These resulting ions are passed through a series of apertures into a high vacuum analyzer where the isotopes of the elements are identified by their mass to charge ratio. The intensity of a specific peak in the mass spectrum is proportional to the amount of the elemental isotope from the original solution. The neutron activation analysis technique involves irradiation of the samples in a neutron flux position of a nuclear reactor, leading to the formation of radionuclide whose radioactivity is measured by high-resolution gamma ray spectrometry. The non-destructive technique (INAA) has many advantageous characteristics like high analytical sensitivity, improved detection limit and negligible matrix effect.

The present work was planned with the objective to analyze the different brands of ballpoint pen inks available in Indian market so as to assess their inorganic element profile. Twenty-two ink samples from different brands and models were analyzed by ICP–MS. Experimental findings showed the absence of all the rare-earth elements in the normal varieties of ballpoint ink. Thirteen rare-earth elements, based on suitable availability and technical considerations were selected as taggants for blue ballpoint pen inks. As ink formulation is organic in nature, for ensuring better homogeneity 13 rare-earth thenoyltrifluoroacetonate chelates (taggant(s)) were prepared.

The aim of this study is to see the efficacy of homogeneous mixing of inorganic taggants with blue ball point ink with the objective to establish linear relation of intensity (signal) against concentrations/amounts of taggant(s) and to derive the minimum detection limit, by inductively coupled plasma–mass spectrometry (ICP–MS) and instrumental neutron activation analysis (INAA). The purpose of the present study is also to develop a reliable, rapid and accurate analytical method for the detection of rare-earth (REEs) taggants in blue ballpoint pen ink. The feasibility study of determination of rare-earth elements in blue ballpoint pen ink tagged with rare-earth thenoyltrifluoroacetonates was also examined. The results obtained can lead to relative/absolute age determination of ink, which is still an unsolved problem to document examiners. However, it is to be understood that this method is aimed at the use of specially tagged inks for use in sensitive documents.

2. Materials and methods

2.1. Sampling

Samples of different varieties (brands, models) of blue ballpoint pen inks were collected from Indian market and local ink manufacturing company and are listed in Table 1 (local ink manufacturing company provided the information of date of production of ink).

2.2. Reagents and preparation of standards

Oxides of rare-earth elements were of 99.99% pure. Standard stock solution (1 mg/ml) of rare-earth elements was prepared by dissolving a calculated amount of high purity oxide in 1 ml nitric acid and making up to 250 ml with deionized water. Further solutions were prepared by diluting the stock solutions of each element in 2% (v/v) HNO_3 with deionized water. Deionized water was produced by EASY-pure RF compact ultrapure water system (18.3 MΩ cm).