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Forensic application of total reflection X-ray fluorescence spectrometry for elemental characterization of ink samples

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ABSTRACT

The possibility of applying Total Reflection X-ray Fluorescence for qualitative and quantitative differentiation of documents printed with rare earth tagged and untagged inks has been explored in this paper. For qualitative differentiation, a very small amount of ink was loosened from the printed documents by smoothly rubbing with a new clean blade without destroying the manuscript. 50 µL of Milli-Q water was put on this loose powder, on the manuscript, and was agitated by sucking and releasing the suspension two to three times with the help of a micropipette. The resultant dispersion was deposited on quartz sample support for Total Reflection X-ray Fluorescence measurements. The Total Reflection X-ray Fluorescence spectrum of tagged and untagged inks could be clearly differentiated. In order to see the applicability of Total Reflection X-ray Fluorescence for quantitative determinations of rare earths and also to countercheck such determinations in ink samples, the amounts of rare earth in painted papers with single rare earth tagged inks were determined by digesting the painted paper in $HNO_3/HClO_4$, mixing this solution with the internal standard and recording their Total Reflection X-ray Fluorescence spectra after calibration of the instrument. The results thus obtained were compared with those obtained by Inductively Coupled Plasma Mass Spectrometry and were found in good agreement. The average precision of the Total Reflection X-ray Fluorescence determinations was 5.5% (1σ) and the average deviation of Total Reflection X-ray Fluorescence determined values with that of Inductively Coupled Plasma Mass Spectrometry was 7.3%. These studies have shown that Total Reflection X-ray Fluorescence offers a promising and potential application in forensic work of this nature.

1. Introduction

The chemical examination of the inks used in printing important historical manuscripts, currency notes, art of work, etc. is very important with respect to their restoration, certification of their authenticity and to know the time of printing or its age [1–3]. In routine examination of the ink samples, parameters such as color, luminescence and absorption of radiation are determined by the microscopic and optical techniques. However, elemental characterization of the ink samples can differentiate different types of inks in a more objective way. This study can give information about the type of ink used in printing the documents and thus can be helpful in restoration of the damaged manuscripts, paintings, etc. If a policy is made by the Government/Printing Agencies to print the important documents tagged with one particular unique element each year, the non-destructive elemental characterization can be used to differentiate the important documents e.g. currency notes, judicial stamp papers, etc. printed in different years. For such differentiation, the elements used for tagging of ink samples should not be present in the commercially used inks and the analytical techniques used for such differentiation should require very small amount of ink sample for the elemental characterization in a non-destructive way. Rare earths are normally not present in commercially available inks and, therefore, tagging with rare earths can be beneficially used for such applications. Inks to be used for printing of documents in a particular year can be suitably tagged with a particular set of rare earths and the tagging elements can be changed every year in a confidential way. Analytical techniques e.g. Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), Paper Chromatography, Thin Layer Chromatography (TLC), High Performance Thin Layer Chromatography (HPTLC) can analyze the trace elements present in the ink samples [3–5] but have certain disadvantages as these are destructive techniques and require large amount of samples. Though Neutron Activation Analysis (NAA), X-ray fluorescence (XRF), Proton Induced X-ray Emission (PIXE) Spectroscopy, Raman spectroscopy etc., can be used for the determination of rare earths in a non-destructive

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way, NAA is not easily accessible to all the laboratories and XRF/PIXE detection limits are comparatively poor [1,6–12]. Total Reflection X-ray Fluorescence (TXRF) spectrometry is a multi elemental analytical technique requiring very small amount of sample and can be beneficially exploited for such applications [13–16]. In the present study, a simple, fast and nearly non-destructive TXRF method for qualitative differentiation of the manuscripts printed with rare earth tagged and untagged ink samples has been developed. In order to see the applicability of TXRF for quantitative determinations of rare earths and also to countercheck such determinations in ink samples, the papers painted with rare earth tagged inks were digested in $HNO_3/HClO_4$ and the rare earths in these solutions were determined by TXRF. The results thus obtained were compared with those obtained by Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

2. Experimental

2.1. Sample preparation

A commercially available ink product free of rare earth elements was used for the present study. This ink sample was tagged with rare earths La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu in the form of their thenoyltrifluoroacetonate complexes in such a way that the approximate concentration of these rare earths in the ink sample was 500 ppm [3]. Manuscripts printed by both the ink samples — tagged and untagged, were used for this study. Three methods of sample preparation labeled as methods A, B and C, were assessed for their feasibility for the differentiation of manuscripts printed using the two ink samples by TXRF. In method A, a small portion of the printed paper, covering a few letters in the area of about 4 mm^2, was cut and pasted at the center of quartz sample support in such a way that the ink on paper faces the X-ray beam when loaded in TXRF spectrometer and the TXRF spectrum was measured. In methods B and C, small portions of the ink on printed papers were rubbed very smoothly with the edge of a new, clean and sharp edged blade without damaging the document and thus loosening a few ng of the ink in the form of fine powder. In method B, 50 μL of 1.5% suprapure nitric acid was put on the loosened fine powders of the ink, sucked and dispensed off at same place 3–4 times with the help of a micropipette. In method C, samples were prepared in a similar manner, as that in method B, except for using Milli-Q water instead of suprapure nitric acid. Finally, the resulting suspension was deposited on quartz sample support (in both methods B and C) and TXRF spectra were measured.

For the calibration of the TXRF spectrometer, single element stock solutions of La, Pr, Nd, Sm, Eu and Gd were prepared by dissolving their respective high purity oxides in suprapure nitric acid in such a way that the concentration of each rare earth element was 100 μg/mL. Merck certiPUR Cobalt ICP standard having a concentration of 1000 μg/mL diluted to 50 μg/mL using 1.5% suprapure nitric acid in Milli-Q water was used as internal standard. Three sets of calibration solutions namely STD-1, STD-2 and STD-3 were prepared by mixing (La, Nd, Gd + Co), (Pr, Eu + Co) and (Sm + Co), respectively in different volumes as given in Table 1. The relative sensitivity of each lanthanide w.r.t. Co was calculated using the four TXRF measurements. For quantitative determinations of the rare earths, 20 mg weights of different ink samples tagged with single rare earths viz. La, Pr, Nd, Sm, Eu and Gd were put on separate blank papers and spread in a circular area of 10–15 mm in diameter. The painted papers, after drying, were digested in $HNO_3/HClO_4$ mixture and the volume of the solution was made up to 5 mL with 1.5% suprapure HNO_3. Two mL volume of this solution was mixed with 1 mL of Co internal standard (Co = 1 μg/mL) for quantitative determination of rare earths by TXRF.

2.2. Instrumentation

An ITAL STRUCTURES total reflection X-ray fluorescence spectrometer TX-2000 was used for these studies. The Cu K_α radiation (8.047 keV) produced at 40 kV and 30 mA in a copper target X-ray tube and monochromatized by W-C multilayer was used for X-ray excitation of the samples. The instrument was calibrated using three sets of rare earth calibration solutions described above. For quantitative determinations of rare earths in painted papers, 10 μL aliquots of their digested solutions mixed with Co internal standard were deposited on two quartz sample supports and TXRF spectra were measured twice by loading the supports in twelve position sample chamber of the TXRF spectrometer for sequential measurement using a live time of 1000 s. The precision of the measurements was determined by taking the average of the two measurements on each specimen of every sample. The X-rays were detected with a Si (Li) detector having a resolution of 139 eV (FWHM) at 5.9 keV (Mn K_α). The X-ray spectra were acquired and processed by computer programs TXRFACQ-32 and EDXRF-32 respectively, provided with the instrument. For ICP-MS determination of rare earths the samples were diluted to a volume of 100 times with milli-Q water and the rare earths elements were determined using a VG PQ EX Cell, Thermo Elemental, UK ICP-MS spectrometer in conventional way using the experimental conditions given in Table 2.

3. Results and discussion

3.1. Qualitative differentiation

TXRF spectra of the tagged and untagged ink samples measured using method A of sample preparation were not distinguishable clearly whereas those measured by using methods B and C could be clearly distinguished from each other. In method A, since a large amount of matrix in form of paper is present on the sample support, it increases the background and makes detection of elements in trace amounts, especially rare earths for which Lα lines are detected, very difficult. Moreover, since a portion of the manuscript is cut and taken

Table 1
Concentration and relative sensitivity values of L-lines of rare earth elements present in different calibration solutions.[a]

Calibration Solution	Elements	Corresponding rare earth L-characteristic X-ray energies (keV)					Volume taken (μL)	Concentration (μg/mL)	RS[b]
		$L\alpha_1$	$L\alpha_2$	$L\beta_1$	$L\beta_2$	$L\gamma_1$			
STD-1	La	4.651	4.635	5.043	5.384	5.789	100	25	0.104 ± 0.009
	Nd	5.230	5.208	5.722	6.090	6.602	100	25	0.14 ± 0.01
	Gd	6.059	6.027	6.714	7.102	7.788	100	25	0.217 ± 0.001
	Co						100	12.5	1
STD-2	Pr	5.034	5.014	5.489	5.850	6.322	100	33.3	0.142 ± 0.007
	Eu	5.846	5.816	6.456	6.842	7.478	100	33.3	0.218 ± 0.008
	Co						100	16.7	1
STD-3	Sm	5.636	5.609	6.206	6.587	7.180	100	50	0.172 ± 0.007
	Co						100	25	1

[a] The calibration solutions were prepared by mixing rare earth single element solutions having concentration of 100 μg/mL and Co solution having concentration of 50 μg/mL.

[b] Relative sensitivities of Lα lines $\pm 1\sigma$, ($n = 4$) w.r.t. Co.