

# The Development of X-Ray Fluorescence for Trace Evidence Detection and Documentation Analysis in Forensic Science

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## Abstract

X-ray fluorescence (XRF) is a non-destructive technology for quick multi-element analysis that requires minimal sample preparation. The spectra obtained by X-ray excitation can supply us with information complementary to those from other wavelengths. In recent years, the rapid advancement of XRF devices has led to an improvement in resolution, delivering better precision and accuracy. In addition, relevant XRF-based devices and methodologies have been developed for numerous applications. For example, portable X-ray fluorescence (PXRF) detectors make compositional information of evidence readily available by enabling on-site detection at crime scenes. There are several studies that use XRF in forensic science research, especially involving trace evidence and questioned documents. Common trace evidence includes glass, soil, fiber, hair, paint, gunshot residue, and explosives. Questioned document frequently involve coins, ink, and paper. The element compositional profile of the evidence helps to trace the source of the evidence. Furthermore, it can also be checked against standards to determine whether the analysis results are consistent. These studies are summarized to demonstrate the discriminating power of elemental analysis by XRF. XRF is likely to be increasingly explored and developed for forensic science applications in the future.

**Keywords:** *forensic science, trace evidence, questioned documents, X-ray fluorescence (XRF), meta-analysis*

## Introduction

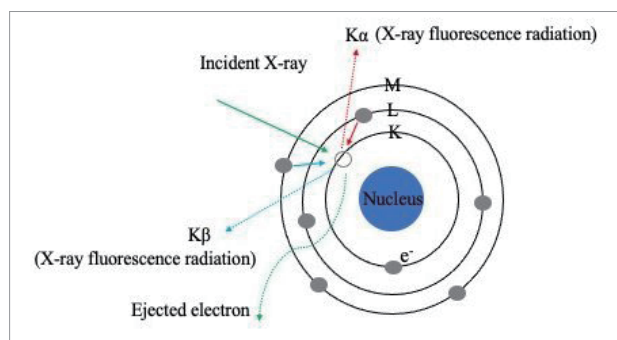
X-ray fluorescence (XRF) is an elemental analysis technique suitable for forensic applications. This technique irradiates samples with high-energy X-ray to eject core electrons from an atom. As a result, an electron with higher energy from the outer orbital will fill the emptied orbital and release energy in the form of photons, thereby emitting fluorescence. The energy of the fluorescence emitted by this electron is distinct

for each element, hence it is called the characteristic X-ray of the element. By detecting these characteristic fluorescence, it is possible to identify a specific element. The principle of XRF is shown in Fig. 1 [1]. Finally, an instrument analyzes the energy and intensity of the characteristic signals to identify and quantify each element. The X-ray source for conventional XRF is an X-ray tube or a sealed radionuclide source (<sup>55</sup>Fe, <sup>238</sup>Pu, <sup>241</sup>Am). XRF has several advantages, including speed, non-destructiveness, minimal sample preparation, and

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extensive element detection, allowing it to be used in a wide range of applications. In addition, XRF can be used in combination with other techniques in sequence. However, XRF has a few limitations. It is not suitable for the detection of light elements due to the energy threshold of detection by X-ray spectrometers and the operating principle of XRF precludes it from being used to analyze compounds. Additionally, surface roughness and particle size can also cause measurement errors [2].



**Fig. 1** When an incident X-ray ejects a core electron, an unfilled orbital is left. XRF is emitted when an electron from higher orbitals fill the empty core orbital. We can see two possible events: The energy of the X-ray fluorescence that is emitted

during a transition from the L shell to the K shell is called  $K_{\alpha}$ ,  $K_{\alpha} = \Delta E_1 = (E_1 - E_0)$ , while the energy of the X-ray fluorescence emitted during a transition from the M shell to the K shell is called  $K_{\beta}$ ,  $K_{\beta} = \Delta E_2 = (E_2 - E_0)$ .  $K_{\alpha}$ , where K indicates the origin of the electron hole and  $\alpha$  indicates that the electron fell from one shell above the electron hole. If the cascading event is from  $n = 3$  (the M shell) to  $n = 1$  (the K shell), it is  $K_{\beta}$ , and so on.  $E_0$ ,  $E_1$ , and  $E_2$  represent the energy levels of the electrons of the K, L, and M shells respectively [1].

The X-ray beam diameter of traditional bench-top XRF's is a few millimeters, making it more suitable for larger targets [2]. This microscale size restricts the use of traditional XRF in the analysis of forensic samples such as glass fragments, soil, fiber, and so on [3]. However, with the development of miniature X-ray tubes combined with polycapillary X-ray optics, an XRF beam can now be collimated to a micrometer-sized spot, thereby greatly reduce sample size limitation [2]. XRF can be divided into two types: wavelength dispersion (WDXRF) and energy dispersion (EDXRF). Table 1 summarizes the comparison between EDXRF and WDXRF [1].

**Table 1** A comparison between EDXRF and WDXRF [1].

	EDXRF	WDXRF
Principle	A complete spectrum of dispersion is acquired virtually instantaneously and can cover a large portion of the periodic table.	Characteristic X-rays are scanned and analyzed sequentially as a point-by-point acquisition.
Resolution	150–300 eV or more	~5 to ~20 eV
Signal-to-noise ratios	Low	Higher (leads to lower detection limits)
Optical components	No	Yes
Ease of use	Easy	Complex
Cost	Inexpensive	Expensive
Speed	Rapid	Slow

For the analysis of small samples, a micro-XRF spectrometer uses either highly collimated or capillary-focused X-ray beams to focus primary radiation to the micrometer range. Both the micro-XRF and scanning electron microscope/energy dispersive X-ray spectrometer instruments (SEM/EDS) can detect characteristic X-rays emitting from samples for multi-element analysis.

Both have good spatial resolution and are non-destructive. The difference between the two instruments is that micro-XRF absorbs X-rays to excite core electrons, whereas SEM/EDS absorbs electron beams and requires samples to be analyzed under vacuum. In addition, micro-XRF instruments generally have larger sample chambers and are more sensitive than SEM/EDS instruments,

because SEM/EDS can only detect minor and major elements at concentrations greater than 0.1% [4-6]. Micro-XRF instruments normally produce a 2D image but with a confocal setup where the confocal point on the sample is scanned in x–y–z directions, they can provide a 3D elemental distribution. This is also known as 3D-XRF. Since only the confocal point is detected, the confocal setup can reduce background intensity [6-8].

Total reflection X-rays fluorescence (TXRF) differs from conventional energy-dispersive XRF mainly in the geometry of excitation where small incidence angles below the critical angle of total reflection are used. Therefore, the X-ray does not penetrate far into the substrate in TXRF, resulting in high signal-to-noise ratio and low detection limits (femtogram levels, picograms per gram concentrations, 108 atoms/cm<sup>2</sup> of metal contamination detectable on wafer surfaces) [9]. The high sensitivity of TXRF, allows the technique to be applied to minute amounts of samples, as low as nanogram, ng/l, and nanometer thick layers [10]. TXRF has several benefits, such as quick processing, a high signal-to-noise ratio of the spectrum, low detection limits (ng/ml and below), high reproducibility, and the need for only very small sample sizes (from µg to ng). It also does not have matrix effects. Moreover, TXRF quantification requires only a single internal standard [11]. However, a drawback of TXRF is that overlapping peaks can complicate quantification when the surface concentration is very low (ng/cm<sup>2</sup>). In addition, meticulous optical alignment is needed, with small shifts or changes in temperature requiring instrument recalibration. Furthermore, dissolution of the sample is required, rendering the technique no longer non-destructive [12, 13].

For unknown samples at a crime scene, portable (or handheld) XRF can be used for rapid on-site/in-situ analysis. Compared to other chemical analysis instruments, portable X-ray fluorescence (PXRF) has poorer precision, accuracy, and detection limits, but its convenience, affordability, minimal sample preparation, and non-destructiveness are features that are very attractive. Traditional chemical analysis techniques, such as ICP-AES, ICP-MS, and AAS, are more time-consuming and expensive, and most of them are destructive [14].

XRF can only evaluate approximately a few squared millimeters of sample area and occasionally, these spots do not represent the complexity of the material. The X-ray beam of scanning macro X-ray fluorescence (MA-XRF) can scan a broad region to address this problem. It can collect millions of data points to build elemental distribution maps [15]. MA-XRF scans over thousands of squared centimeters during a single test. MA-XRF is often utilized in the authentication of paintings [16].

The use of high-energy synchrotron radiation as an X-ray excitation source can boost sensitivity, precision, accuracy, and resolution. It is appropriate for the analysis of heavy elements in trace samples [17]. For low concentrations and small samples, traditional equipment is constrained by a detection limit. Synchrotron radiation can be utilized to improve discriminating power. Synchrotron radiation X-ray fluorescence (SR-XRF) is a promising technique for the identification of trace evidence. However, its exorbitant cost and low accessibility prohibits its employment as a routine identification procedure for forensic investigations [18]. The comparison of various XRF techniques is summarized in Table 2.

**Table 2** A comparison of various XRF.

Types	Advantage	Drawback
Conventional XRF	<ul style="list-style-type: none"> <li>▶ Suitable for large samples</li> </ul>	<ul style="list-style-type: none"> <li>▶ Diameter of the beam is approximately a few mm, limiting the detection of small samples.</li> </ul>
Micro-XRF	<ul style="list-style-type: none"> <li>▶ Good spatial resolution</li> <li>▶ Sensitive, Accuracy</li> <li>▶ Suitable for small samples (mm-µg)</li> </ul>	
TXRF	<ul style="list-style-type: none"> <li>▶ Suitable for minute samples (nanogram)</li> <li>▶ Rapid processing</li> <li>▶ High signal-to-noise ratio of the spectrum</li> <li>▶ Low detection limits</li> <li>▶ High reproducibility of results</li> <li>▶ Lack of matrix effect</li> <li>▶ Only one internal standard is sufficient for quantification</li> </ul>	<ul style="list-style-type: none"> <li>▶ Overlapping peaks</li> <li>▶ Calibration is complicate</li> <li>▶ Samples need dissolution</li> </ul>

Types	Advantage	Drawback
<b>PXRF</b>	<ul style="list-style-type: none"> <li>▶ Rapid</li> <li>▶ On-site/In-situ</li> <li>▶ Affordable</li> </ul>	<ul style="list-style-type: none"> <li>▶ Poorer precision, accuracy, and detection limits</li> </ul>
<b>MA-XRF</b>	<ul style="list-style-type: none"> <li>▶ Can scan a large area, unlike other XRF just analyze a few spots</li> </ul>	
<b>SR-XRF</b>	<ul style="list-style-type: none"> <li>▶ Suitable for the analysis of heavy elements</li> <li>▶ Good discriminating power</li> <li>▶ High sensitivity, precision, accuracy, and resolution</li> </ul>	<ul style="list-style-type: none"> <li>▶ High cost</li> <li>▶ Limited accessibility</li> </ul>

XRF has a wide range of applications. This review will focus on examining the application of XRF in the identification of trace evidence and documents in recent years.

## The Application of XRF to Trace Evidence

### Glass

The brittle and transferrable qualities of glass make it valuable for establishing a link between its collection from a suspect and its appearance at a crime scene, such as in a hit-and-run, burglary, or shooting. Refractive index (RI) analysis is the most popular approach for glass identification. If the glass cannot be identified using RI, then techniques such as SEM/EDS, micro-XRF, Laser Induced Breakdown Spectroscopy (LIBS), ICP-MS, and LA-ICP-MS are employed for elemental analysis, which provide more information when comparing the glass samples with each other. Moreover, it can be used to identify the source of the glass maker [19, 20].

In recent years, the Organization of Scientific Area Committees (OSAC) has approved several standard methods for glass analysis, one of which is “micro-XRF...for the identification of glass in forensic analysis (E2926-17) “ [21, 22]. X-ray energy is powerful and it can penetrate deeply into glass with better detection limits [20]. According to the OSAC Research Needs Assessment Form, contemporary micro-XRF systems use SDD detectors with improved sensitivity and accuracy instead of conventional SiLi detectors. Although micro-XRF can analyze small (0.3–0.5 mm or 50–200 µg) and irregularly shaped particles, a flat surface is necessary to give more precise and accurate quantification. As a

result, an irreversible procedure is necessary to embed irregularly shaped particles into resin and polish them to produce a flat surface. Additionally, the size and form of the known and questioned samples must be matched to attain greater precision and accuracy [19, 23]. PXRF can be used as an in-situ preliminary scanner for glass examination to obtain information immediately. One study used PXRF to discriminate 98.31% of 7,500 pair-wise comparisons created from 25 glass samples [24]. Funatsuki et al. examined 75 samples using a combination of RI analysis, XRF, and X-ray absorption fine structure (XAFS) spectroscopy. The concentrations of CeO<sub>2</sub>, MgO, Al<sub>2</sub>O<sub>3</sub>, and K<sub>2</sub>O, the amplitude of the XAFS spectra, and the intensity of the Fourier transform were used to identify three car window glass manufacturers [25]. For glass samples that cannot be distinguished by RI analysis, high-energy SR-XRF, with its high sensitivity and low detection limit, can be used to analyze trace elements in glass samples for identification [17, 26].

### Soil

Soil is complex and diverse, including various organic and inorganic components. Soil evidence is typically found on shoes and tires related to the suspects and it establishes a link to the geographical context of the location where a suspect passed [27]. In a tomb theft case, the examination and comparison of the soil composition between the tools used by the perpetrators, the stolen antique, and the tomb might be undertaken to reconstruct the crime. Common soil analysis comprises color analysis, elemental analysis, mineral analysis, and particle size analysis. Elemental composition analysis can use non-destructive XRF to compare elemental composition between various samples [28]. Conventional

micro-EDXRF is quick, spatially resolved, and provides qualitative multi-element analysis, whereas 3D confocal micro-EDXRF yields a three-dimensional elemental distribution. Each has its own unique advantages, allowing higher dimensional information to be available when studying soil particles [29]. In a study of various Australian soil samples, XRF data indicated that concentrations of iron are the most distinguishable. In addition, a comparison of the elemental distribution of these soils by different instruments showed that the discrimination power of LIBS was 92.4%, XRF was 98.5%, and that of SEM/EDX was 99.5%, which showed that the analysis of XRF was highly sensitive [30]. SR-XRF with high-energy X-rays (116 keV) has the advantages of precision, and transmission, and it is suited for the analysis of heavy elements in trace samples. The compositions of heavy elements have geographic peculiarities, and SR-XRF is suitable for the assessment of soil origin. However, soil analysis is complex and encompasses a wide range of subjects, requiring greater training and skill to analyze soil data. In recent years, Japanese researchers have sought to develop a database of soils that can be used to swiftly compare and identify samples and improve data interpretation [31, 32].

### ***Fiber and Hair***

Fiber is less typically utilized for elemental analysis. However, micro-XRF and TXRF can provide good sensitivity for the elemental analysis of a single fiber. They can handle minute solid materials, such as single fibers as tiny as 5 mm and 2 mm in length, respectively [33]. Non-destructive SR-micro-XRF with vertical focusing can be utilized to investigate a single polyester garment fiber. For identifying elements in a single fiber, SR-micro-XRF with a vertical concentrated beam is substantially more sensitive than SR-XRF with an unfocused beam [34]. Moreover, the combination of numerous instruments can further boost discriminating capacity, as shown in a research on fake leather that employed micro-FT-IR, microspectrophotometry, and XRF to distinguish about 92% of 15,576 pair-wise comparisons [35].

Asbestos is often used in construction and flame retardant materials because of its fire and its heat resistance properties and light weight [36]. However, medical studies have pointed out that asbestos is carcinogenic [37]. Therefore, asbestos has been controlled

and prohibited in several countries. A study was undertaken to rapidly determine the presence of asbestos-containing materials in construction debris using micro-XRF elemental mapping [38].

Poly[ (benzo-[1,2-d:5,4-d']-benzoxazole-2,6-diyl)-1,4-phenylene] (PBO) fiber is a high-performance heat-resistant fiber with high strength, suitable for using in soft-body armor. Nevertheless, many scholars suspect that residual phosphoric acid may degrade the benzoxazole ring important to the properties of PBO fiber, thereby reducing its effectiveness for ballistic protection. A study used XRF to analyze the presence of residual phosphoric acid in PBO fiber [39].

In recent years, the rising focus on sustainability has led to the creation of novel eco-textile materials. Therefore, it has become vital to detect poisonous, allergenic, and carcinogenic substances in textile products. For digested textile samples, TXRF is an appropriate tool for the fast identification of these components. The TXRF spectrum is viewed as a fingerprint and it has great discriminating power [40].

Hair evidence is easy to obtain, and sample preparation is simple. In a number of studies, hair is often tested for toxic, carcinogenic, and metallic elements such as Fe, Pb, Br, As, Hg, K, Ni, Zn, and Cu. XRF can be used to analyze the concentration of ingested toxins, and these trace elements in hair can be seen as bioindicators to assess whether sample donors have been exposed to environmental pollution, dietary problems, or disease in criminal cases [41-46].

### ***Paint***

In criminal cases, paint is crucial evidence that is often transferred during collisions. In hit-and-run cases, it is crucial to distinguish whether the questioned paint at the scene matches the standard paint on the vehicle and to link the paint to information such as the manufacturer, year of manufacture, and the model of the vehicle [47]. Additionally, at the scene of a burglary, the paint on the tools used to break doors and windows can be transferred to other objects at the scene. However, when collecting paint samples, it is important to note that the paint on one vehicle may vary from location to location [48]. Consequently, sampling should be done close to the impacted area. Inorganic pigments can be analyzed by XRF for elemental composition. XRF can penetrate nine layers, with individual layers up to 280  $\mu\text{m}$  in thickness

being suitable for analysis [49]. Several studies have demonstrated that it is possible to use various analytical instruments to distinguish the source of paints of the same color between different manufacturers [50, 51]. Furthermore, analysis done by another study has found batch-to-batch variation for paints of the same brand and type, meaning paints produced from the same factory at different times can also be distinguished [52].

However, the drawback of XRF is that the diameter of the X-ray spot size is usually not small enough (approximately a few millimeter) to allow cross-sectional analysis. For this reason, unless each layer of paint is physically separated, it is difficult to gather precise information. Regardless, this technique is time-consuming and damaging. Micro-XRF can provide a spatial resolution of 50  $\mu\text{m}$ , which helps to address this challenge [53]. Moreover, high-energy synchrotron excitation can be employed as a source for confocal micro-XRF. By focusing on the diameter of the high-energy X-ray beam, the detection limit can be lowered, and the sensitivity is enhanced compared to typical micro-XRF. The improved depth resolution gained can aid in elemental depth profiling analysis of multi-layer paint samples, the detection of the structure of each layer of the sample, and providing precise elemental distribution of each layer. Raman and FT-IR spectra can provide information on each paint layer without the requirement for damaging processing of the paint sample. These tools complement each other by analyzing for distinct features of the paint and improving discrimination power [54-58]. XRF has been used with instruments such as Raman spectroscopy, FT-IR, and SEM/EDS to provide multi-aspect information on a questioned paint sample to determine the source of automobile paint [59-61].

### ***Gunshot Residue***

In a shooting crime scene, the gunshot residue (GSR) on clothing and skin is often used to determine whether the suspect fired the gun. In addition, the color distribution of lead, copper, and nitrocellulose contributes to GSR patterns that help to estimate shooting distance. The closer the distance, the more concentrated the GSR distribution. Furthermore, qualitative and quantitative analyses can be used to categorize the types of ammunition and firearms to narrow down the scope

of an investigation [62]. All these details can be utilized to reconstruct the bullet's trajectory. GSR comes from ammunition, primers, cartridge casings, and barrels. GSR can be split into organic and inorganic components; inorganic GSR has unique properties and can be examined to distinguish the source of the ammunition manufacturer [63, 64]. The usual approach for analyzing inorganic GSR uses SEM/EDS to evaluate particle form and size and to detect individual elements in the particles concurrently. GSRs are spherical in form and typically between 5 and 20  $\mu\text{m}$  in diameter [65]. The characteristic elements that comprise GSR are heavy metal elements, Pb, Sb, and Ba. SEM/EDS has good spatial resolution, but lacks elemental sensitivity compared to other techniques such as XRF [66]. Contamination of a sample with body fluids such as blood can also interfere with GSR identification [65]. One study pointed out that MA-XRF has sufficient sensitivity and selectivity; it can detect the lead signature of a bullet impact even if covered by multiple layers of paint or blood on an X-ray penetrating surface [67].

Recently, with the rise in awareness of environmental pollution, heavy metal-free ammunition has appeared in consumer markets. SEM/EDS characterization of these metal-free ammunitions has been challenging [68]. As a result, the hunt for other particular constituents from other ammunition types and research into organic GSR analysis was undertaken. A study pointed out that the multiple element detection capacity of XRF is promising for the identification of heavy metal-free ammunition [69]. The advantages of utilizing XRF for inorganic GSR measurement are its non-destructiveness, little sample preparation, and capacity to identify elements such as titanium or potassium that cannot be seen with standard color reagents [70]. Conventional XRF cannot produce elemental maps. In its place, millimeter-X-ray fluorescence and micro-XRF can both generate elemental maps to obtain GSR patterns and estimate shooting distance. As a process, m-XRF is faster than micro-XRF, but its resolution is not as great as micro-XRF [71, 72]. Flynn et al. observed that micro-XRF may detect GSR particles on a target if shooting distance is <30 cm but cannot replace SEM/EDS since it cannot detect particles <10  $\mu\text{m}$  in diameter, due to the higher beam diameter [66]. Additionally, TXRF is fast, has high repeatability, is capable of multi-element analysis, and is effective in

detecting GSR collected from skin [65].

### ***Explosive***

Terrorist strikes utilizing explosives can cause very serious injuries. The explosion from a solid or liquid component or mixture, initiated by the right stimulus, rapidly generates a lot of heat, such that surrounding air greatly expands, generating immense pressure that instantaneously releases. Explosives are complicated, contain high-energy chemicals, different additives, and reaction by-products. They differ from brand to brand, and from manufacturer to manufacturer. Among these, additives are specific. Current research utilizes three analytical techniques to differentiate explosives: HPLC-HRMS, XRD, and XRF. The composition of the explosive varies based on its brands, producers, and country of origin. From this information, a database can be established to preserve the compositional information of explosives for easy comparison by investigators [73]. XRF is suitable for detecting explosives and their triggering mechanisms through the examination of the elemental composition of solid samples [74]. For post-explosion scenes, PXRF is a convenient instrument for rapid, on-site, preliminary identification [75]. For protected targets, such as suspected parcels or mail, non-destructive detection is highly critical to assure security and safety. PXRF can identify the metallic elements and hazardous elements of the contents. However, as the thickness of the shield rises, the intensity of the fluorescence of each element in the sample also decreases [76].

## **The Application of XRF to Questioned Document Examination**

### ***Coins***

In recent years, the quantity of counterfeit coin cases has skyrocketed. As counterfeiting tactics get more advanced, it has become more difficult to validate a coin through touch, weight measurement, and visual inspection. Thus, the aid of proper equipment is important to successfully detect and link distinct cases. These strategies can aid with source tracing to locate counterfeit coin producers.

A study was conducted on 89 counterfeit coins (¥500) that were seized in the Aichi Prefecture in 1995

from two different hotels and banks. XRF can first accomplish a non-destructive elemental analysis to classify these counterfeit coins according to the content of their six major constituent elements (Cu, Ni, Fe, Zn, Mn, and Cr). In addition, a metal microscope can observe many bent micro-structures at the positions of a letter, figure, and at the edge of the coins after chemical etching to evaluate their manufacturing process [77]. 3D-XRF was used to analyze the authenticity of two ancient Chinese coins. 3D-XRF can perform depth-selective analysis to gather information on the distribution of elements inside the samples. By studying the depth distributions of Fe, Ca, and Cu, the authenticity of two ancient Chinese coins can be established [78].

The main goal of employing XRF to identify genuine and counterfeit coins is to detect the difference in elemental content of the coating metal on the counterfeit coins. XRF can also be used to evaluate the development of new counterfeiting technology. Consequently, real coins can be created with enhanced materials and procedures to make them more identifiable in the future. Additionally, precious ancient coins typically employ XRF to assess their age, which can be useful in archaeological studies [79-85].

### ***Ink***

Ink analysis is fairly comprehensive. Ink can comprise pencils, ballpoint pens, toner, and pigments. Ink testing by XRF has been applied to artwork, banknotes, stamps, questioned documents, licenses, vouchers, and many other samples to assist identifying the type of ink involved. It is vital to identify the origin, age of the sample, and whether the sample has been altered and whether the authenticity of the sample can be verified [2, 86, 87].

Ink analysis is generally done by microscopic and optical methods for preliminary inspection. Further chemical analysis helps to identify the kind, composition, and manufacturer. However, removing the ink from the page with solvent extraction is occasionally required, although harmful. PRAXIS is a new mobile instrument that combines  $\mu$ -XRF and  $\mu$ -Raman. All elements heavier than Mg ( $Z = 12$ ) were studied by XRF, whereas Raman spectroscopy analyzed complex molecules [88, 89]. However, some elements in the paper can interfere with ink detection, therefore care must be taken when using XRF[88]. Moreover, IR, Raman, and XRF techniques complement each other, giving increased

distinguishability for the identification of inks with the same color but different compositions. IR analysis can offer data on the principal dyes, resins, and oily liquids; Raman spectroscopy can directly and non-destructively identify the inks; XRF provides elemental information [90]. In the ink of crucial documents, e.g., currency notes and judicial stamp papers, rare earth elements can be marked to help determine the year of creation.

TXRF is a multi-element analysis approach, and just a small amount of sample is needed. Qualitative and quantitative identification of inks can be done on rare earth elements [11, 86]. XRF is a promising technology for elemental analysis in inks, and it has good identification capabilities in most studies.

For XRF applications on artwork, synchrotron radiation-induced MA-XRF can produce small beam spots with great resolution and sensitivity. It can be coupled with other tools, such as SEM-EDS, and FT-IR, to detect pigments on a picture and to assess authenticity [91]. Micro-elemental XRF's mapping capacity can offer the distribution of elements in paintings, manuscripts, jewelry, pearls, and porcelain, which aids in the understanding of the manufacturing process, the materials used, and the determination of origin and age [4, 81, 92, 93].

Revenue stamps and postage stamps, which are attached to papers to collect taxes or fees by the government, contain sophisticated designs and features on them for anti-counterfeiting. ED-XRF spectroscopy is rapid, simple, and cost effective and has been utilized to display elemental profiles of Brazilian revenue stamps. Among these, Ti and Ca are the key identifiers, which can be utilized as indications to identify between real and counterfeit revenue stamps [94]. Several studies have also been undertaken utilizing XRF to study the characteristic inorganic pigments on postage stamps to assist the detection of genuine or counterfeit products [95-98].

In document identification, the chemical composition of the ink in copied papers is studied. The study of this composition enables us to determine the difference between a suspicious document and an actual document, and potentially can link the printer to a certain manufacturer and model, thereby reducing the field of criminal inquiry in fraud cases. There are two types of printers: laser printers and inkjet printers. The former utilizes toner while the latter uses ink. In a study, micro-

XRF was used to assess nine distinct models of laser copiers. The toner samples were collected from the toner cartridge, and from the printed sample surface, both in-situ and ex-situ. The discriminating powers were 94.4%, 75%, and 69.4%, respectively [99]. Furthermore, the combination of FT-IR and XRF can improve the discriminating power of black powder toners compared to individual use toners [100, 101].

Counterfeiting banknotes is a big financial crime. To protect the economy from being affected by counterfeit currency, banknotes or bills in many countries have many anti-counterfeiting features embedded in them. The identification of ink is an important point. PXRF was utilized in various investigations to directly measure different color regions on the same sample without pretreatment. Qualitative and semi-quantitative examinations of elemental concentrations were done to identify the discrepancies in the compositions of real and counterfeit banknotes [102-104]. When using micro-XRF, it is important to note that X-rays can penetrate the banknote and may detect the elements on the back of the banknote [105].

### *Paper*

Paper is quite extensively used, and there are many distinct types of paper. In the case of antique artwork, it is useful to know the variety of paper used for restoration. In forensic science, envelopes, notes, contracts, and photo sheets are evaluated to determine the kind, material, and maker of the paper, which helps to guide the direction of an inquiry. For example, in a suicide case, if the type of paper used to write the suicide note is different than the type the deceased was accustomed to using, and there is no paper of the same material in the immediate vicinity, the case may be ruled a homicide.

There are several physical and chemical approaches for the analysis of papers. A research of twenty-five different multifunctional office papers from the European market shows that XRF has remarkable discriminating skills. The non-destructiveness of XRF is a big advantage. However, a relatively large paper sample (surface area of 7.1 cm<sup>2</sup> in the study) is required, and the sensitivity is relatively inferior compared to other instruments [106]. WDXRF was used to perform qualitative and semi-quantitative analyses on 29 types of paper, newspaper, filter paper, inkjet paper (photo



quality), photo paper, carbonless copy paper, and printing paper in six categories to effectively differentiate the categories of paper and different brands of printing paper. However, in this investigation, it was impossible to discriminate between papers made by the same manufacturer or from the same batch [107]. Additionally, the identification of the age of paper and the ink of writing is an important direction of contemporary research. Yet, due to the intricacy of the variables involved, ambiguity and rough estimations persist in these analytical results.

### **Summary**

Due to admissibility considerations and the important nature of physical evidence in the court, it is desired that samples from the crime scene are changed as little as possible during investigations. Hence, the choice of instruments is very critical in evidence characterization. Minimal sample preparation and non-destructive methods are deemed desirable. Usually, spectroscopic and microscopy analyses are done initially, followed by chemical analysis for additional inspection. When other non-destructive method is difficult to gather enough information to identify the sample, elemental analysis is an excellent supplemental identification method. The non-destructive, quick, accurate, and precise qualities of XRF can give spatially resolved elemental data of samples to boost discrimination power.

Trace evidence, documents, and other evidence in a number of studies using micro-XRF, 3D-XRF, TXRF, PXRF, and MA-XRF techniques showed that each has its own advantages and disadvantages. Each has various applications. In the author's perspective, there are certain aspects that need to be improved in the future. From the foregoing literature, it can be observed that the combination of XRF with other instruments can strengthen the discriminating capacity of physical evidence. As for how the combination can effectively boost discrimination, we need to rely on further studies to develop standard operating procedures. Due to the scarcity of physical evidence at the crime scene, and the desire for evidence preservation and short processing time, it is advised that a set of ideal processes for evidence analysis be devised.

In addition, a growing number of different databases are likely to be built and linked in the future. Information from chemical analysis of physical evidence in the

laboratory, such as soil composition in different regions, paints of various brands, banknotes of various countries, etc., and elemental analysis results from XRF can be shared between laboratories through the cloud for quick comparison, then various cases can be solved more rapidly.

### **Conclusion**

In conclusion, XRF is a promising tool that can be used in conjunction with other devices and chemical tests to increase the discrimination of materials. In the future, more study on XRF is needed to enhance its advantages and overcome its limits. It is predicted that it will offer more analytical methodologies development to forensic science.

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